ARTIFICIAL WEATHERING REVEALS REDUCED ELEMENTAL LEACHABILITY FROM HARDENED BIOMASS ASH

by

Erwin Rehl

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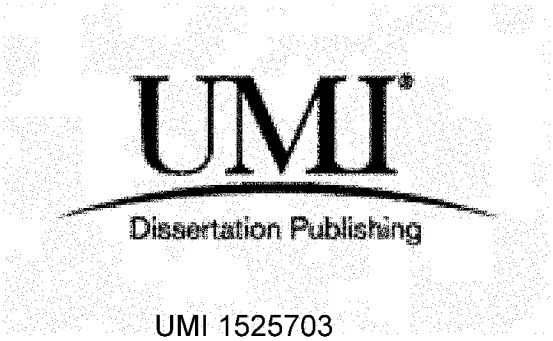

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ABSTRACT

Biomass ashes are potential soil amendments that reduce soil acidity and provide plant nutrients, but trace elements in ash may be leached from the solid phase, thereby posing environmental concerns. We determined the leachability of major and trace elements as influenced by ash pre-treatments, the presence of soil, and the pH of the receiving environment. Weathering was simulated by serial batch extraction where pH was uncontrolled, and by single extraction under controlled pH conditions. We found that hardening reduced the solubility of ash, and reduced the leachability of Al, Ba, Ca, Cu, Mo, Sr, and V, as determined by ICP-MS. In a separate experiment, extractions of ash samples showed that when pH was lowered the leachability of most elements increased while a few decreased. The results of the weathering experiments support the use of ash as a soil amendment.

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GLOSSARY

Acronyms

5%BA	5% Bottom Ash
5%HBA	5% Hardened Bottom Ash
BA	Bottom Ash
BC	British Columbia
BCCSR	British Columbia Contaminated Sites Regulation
CCE	Calcium Carbonate Equivalency
CEL	Central Equipment Laboratory
DW	Drinking Water
DOC	Dissolved Organic Carbon
EC	Electrical Conductivity
EFL	Enhanced Forestry Lab
EPRI	Electric Power Research Institute
FAL	Freshwater Aquatic Life
HBA	Hardened Bottom Ash
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
ICP-OES	Inductively Coupled Plasma Optical Emissions Spectroscopy
L/S	Liquid/Solid Ratio
MAL	Marine Aquatic Life
OD	Oven Dry
OMRR	Organic Matter Recycling Regulations (British Columbia)
ORP	Oxidation Reduction Potential
PAH	Polycyclic Aromatic Hydrocarbons
QA/QC	Quality Assurance / Quality Control
SACoP	Soil Amendment Code of Practice (British Columbia)
UNBC	University of Northern British Columbia
w/w	weight/weight
XRD	X-Ray Powder Diffraction
XRF	X-Ray Fluorescence

Elemental Symbols and Their Names

Symbol	Name	Symbol	Name	Symbol	Name
Ag	Silver	Hg	Mercury	Si	Silicon
Al	Aluminum	K	Potassium	Sn	Tin
As	Arsenic	Li	Lithium	Sr	Strontium
B	Boron	Mg	Magnesium	Te	Tellurium
Ba	Barium	Mn	Manganese	Th	Thorium
Be	Beryllium	Mo	Molybdenum	Ti	Titanium
Bi	Bismuth	Na	Sodium	Tl	Tantalum
Ca	Calcium	Ni	Nickel	U	Uranium
Cd	Cadmium	P	Phosphorus	V	Vanadium
Co	Cobalt	Pb	Lead	W	Tungsten
Cr	Chromium	S	Sulphur	Y	Yttrium
Cu	Copper	Sb	Antimony	Zn	Zinc
Fe	Iron	Se	Selenium	Zr	Zirconium

Mineral Formulas

Name	Formula	Name	Formula
Amorphous Gibbsite	$Al(OH)_{3\ (am)}$	Hydroxyapatite	$Ca_5(PO_4)_3(OH)$
Gibbsite (Soil)	$Al(OH)_3$	Imogolite	$Al_2SiO_3(OH)_4$
Aluminum (III) oxide	Al_2O_3	Kaolinite	$Al_2Si_2O_5(OH)_4$
Basaluminite	$Al_4(OH)_{10}SO_4$	K-Jarosite	$KFe_3(SO_4)_2(OH)_6$
Aragonite	$CaCO_3$	Lepidocrocite	$FeO(OH)$
Barite	$BaSO_4$	Maghemite	Fe_2O_3
Boehmite	$AlO(OH)$	Magnesioferrite	$MgFe_2O_4$
Brucite	$Mg(OH)_2$	Manganite	$MnO(OH)$
Tricalcium phosphate	$Ca_3(PO_4)_{2\ (beta)}$	Magnesiochromite	$MgCr_2O_4$
Calcite (hydrated solid)	$CaCO_3 \cdot H_2O(s)$	Manganese hydrogenphosphate	$MnHPO_4$
Calcite	$CaCO_3$	Plumbgummite	$PbAl_3(PO_4)_2(OH)_5 \cdot (H_2O)$
Chloropyromorphite(c)	$Pb_5(PH_4)_3Cl$	Rutile	TiO_2
Chrysotile	$Mg_3(Si_2O_5)(OH)_4$	Clinocervantite	Sb_2O_4
Cobalt Ferrite	$CoFe_2O_4$	Sepiolite	$Mg_4Si_6O_{15} \cdot 6H_2O$
Cupric Ferrite	$CuFe_2O_4$	Sepiolite (A)	$Mg_4Si_6O_{15} \cdot 6H_2O$
Diaspore	$AlO(OH)$	Tin (I) sulphate	$SnSO_4$
Dolomite (disordered)	$CaMg(CO_3)_2$	Strengite	$Fe(PO_4) \cdot 2(H_2O)$
Dolomite (ordered)	$CaMg(CO_3)_2$	Strontianite	$SrCO_3$
Fluoroapatite	FCO_3-Apatite	Tenorite(c)	CuO
Akaganéite	$Fe(OH)_{2.7}Cl_{0.3}$	Thorium (IV) hydroxide	$Th(OH)_4$
Ferrihydrite	$Fe_2O_3 \cdot 0.5(H_2O)$	Thorium (IV) oxide	ThO_2
Ferrihydrite (aged)	$Fe_2O_3 \cdot 0.5(H_2O)$	Vaterite	$CaCO_3$
Gibbsite (C)	$Al(OH)_3$	Witherite	$BaCO_3$
Goethite	$FeO(OH)$	Yttrium hydroxide	$Y(OH)_3$
Halloysite	$Al_2Si_2O_5(OH)_4$	Yttrium phosphate	$YPO_4 \cdot H_2O$
Hausmannite	Mn_3O_4	Yttrium phosphate	YPO_4
Hematite	Fe_2O_3		

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"Keep calm and carry on" – Winston Churchill

1.0 INTRODUCTION

1.1 Background

Combustion of fossil fuels with the associated greenhouse gas emissions are an increasing environmental concern. Consequently, clean, efficient alternative forms of energy are in demand. One way to reduce the need for fossil fuel combustion is through the use of biomass as fuel. Bioenergy refers to processes whereby heat and/or electricity are generated by utilizing biomass (McKendry 2002a,b). Several types of bioenergy systems exist, which include boilers, pyrolysis systems, and gasifiers. Each of these thermo-chemical processes utilize biological materials derived from living or recently living organisms (as distinct from coal or petroleum). Plant biomass is the most common fuel used in bioenergy systems, chiefly wood products and wood residues.

Gasification is a thermochemical process in which biomass is incinerated with limited amounts of oxygen to create a combustible gas stream; the gas is then combusted in an oxygen rich environment (McKendry, 2002a). Incineration temperature can reach up to 1200°C, depending on the process (McKendry, 2002b). The generated gas stream can be used as a fuel for energy generation, or to provide feed stocks for chemical synthesis, such as liquid fuels generated using the Fischer-Tropsch process (McKendry, 2002a; Isayama and Saka, 2008; Penniall and Williamson, 2009). The product gas, produced by gasification, is generally 40-50% N_2, 15-20% H_2, 10-15% CO, 10-15% CO_2, and 3-5% CH_4 (McKendry, 2002b). The percent range of the product gases from gasification can be attributed to the use of different types of biomass.

During the gasification process almost all of the organic components (e.g. carbon) in the biomass evolve as gas. The leftover residue consists mainly of inorganic elements and very little carbon, and is known as biomass ash. The ash content of woody biomass is 1.6% for aspen, 0.69% for birch, 0.48% for douglas-fir, and 0.53% for spruce (Venner et al., 2011). Furthermore,

Pitman (2006) also notes that bark typically has more ash content than stem-wood; 6% and 0.25% respectively.

Uses for biomass ash, beyond disposal in landfills, have also been found. These include the incorporation of fly ash into cement products (Rajamma et al., 2009; Wang et al., 2008) and internal wall partitions (Leiva et al., 2009). Potential utilization of biomass ash as a soil amendment has also been investigated, but is still an under-researched area. The management and utilization of biomass ashes depends primarily upon its physical and chemical properties.

1.2 Chemical and Physical Properties of Biomass Ashes

Biomass ash can be categorized into two main types, fly ash and bottom ash (Venner et al. 2011; Demeyer et al., 2001; Pitman, 2006). Easily volatilized metallic and non-metallic elements are taken with the gas stream. The formation of fly ash occurs when some of these metallic and non-metallic elements condense (Pitman, 2006). Condensation occurs as the volatilized elements reach cooler surfaces, away from the combustion zone (Pitman, 2006). The condensation results in fly ash that generally contains higher concentrations of so-called "toxic" and "heavy" elements compared to bottom ash. Finally, bottom ash is the residual material that was not converted into the biogas stream (Liao et al., 2007; Augusto et al., 2008; Pitman, 2006).

The volatilization of elements during incineration can occur at different temperatures (Pichtel, 2005). Around 850°C K, Mg, Na, Bi, Cr, Ge, Li, Pb, Sn, Tl, and Zn are volatilized. At 1000°C, Al, Be, Cs, Nb, Sb, Sr, Th, Y, and Zr are volatilized, alongside those elements at 850°C (Pichtel, 2005). Pitman (2006) also states that K and S volatilization occurs above 800-900°C and 1000-1200°C respectively. Elements such as Mg, Zn, Mn, P, and Si show very little change in overall concentration (in bottom ash at different burning temperatures) with changes in incineration temperature. Macro-nutrients (e.g. Ca, K, Mg, S, P) contained within the biomass are

retained at their highest level in the bottom ash materials when burning temperatures are between 500°C and 800°C (Pitman, 2006).

The concentration of elements contained within bottom ash and fly ash can vary due to elements that become volatilized and condense and those that remain. Furthermore, feedstock can also vary this concentration of elements (Table 1.0) (Rehl et al., unpublished; Steenari and Lindqvist, 1997; Steenari et al., 1999; Pichtel, 2005; Liao et al., 2007). The typical elemental compositions of several ashes can be found in Table 1.0.

Table 1.0 – Average elemental composition (shown with standard deviation) of wood fly and bottom ashes and coal fly ashes.

Parameter	Wood Fly Ashes[a]		Coal Fly Ashes[b]		Wood Bottom Ashes[c]	
	Mean	*SD*	*Mean*	*SD*	*Mean*	*SD*
Major Elements						
Al (%)	2.62	2.08	4.95	4.49	2.32	1.00
B (ppm)	750	n/a	367	333	n/a	n/a
Ba (ppm)	1390	156	1198	2070	3087	2607
Ca (%)	17.1	7.7	4.12	4.76	17.0	10.5
Fe (%)	1.44	1.11	3.25	3.06	1.48	0.49
K (%)	6.98	5.14	0.274	0.172	5.73	3.18
Mg (%)	3.10	1.11	0.897	1.439	3.08	0.88
Mn (%)	1.09	0.57	0.015	0.019	1.64	0.98
Na (%)	0.849	0.188	0.570	1.11	1.04	0.24
P (%)	0.661	0.123	0.100	0.015	1.12	0.49
Si (%)	11.9	11.2	4.65	9.48	11.5	2.2
Sr (%)	0.076	n/a	0.056	0.033	0.0371	n/a
Trace Elements						
As (ppm)	41.8	46.6	116	65	24.0	30.0
Cd (ppm)	25.5	15.3	5.05	4.31	14.8	12.9
Co (ppm)	23.0	22.6	13.5	5.5	61.0	76.4
Cr (ppm)	223	179	49.3	31.9	105	47
Cu (ppm)	140	45	63.3	26.2	297	357
Hg (ppm)	0.413	0.421	0.220	n/a	0.124	0.148
Mo (ppm)	19.0	14.9	20.5	18.4	7.50	3.54
Ni (ppm)	99.8	81.4	67.3	86.3	134	68
Pb (ppm)	230	354	58.0	57.8	470	819
Se (ppm)	3.43	2.32	14.2	6.4	0.833	0.208
Zn (ppm)	3577	3073	155	177	2303	2292

[a]*Compilation from wood fly ash articles (Holmberg et al., 2000; Steenari et al., 1999; Rehl, unpublished)*
[b]*Compilation from coal fly ash artilces (Dudas, 1981; Neupane et al., 2012; Talbot, 1978; Theis and Wirth, 1972)*
[c]*Compilation from wood bottom ash articles (Gori et al., 2011; Steenari et al., 1999; Rehl, unpublished)*

Oxides of alkali and alkali earth metals dominate the initial composition of biomass ash. These oxides are then slowly hydrated and/or carbonated through reactions with air (Demeyer et

al., 2001; Pichtel, 2005; Steenari and Lindqvist, 1997). Demeyer et al. (2001) reported that the major compounds found within wood ash are calcite ($CaCO_3$) and lime (CaO). Other constituents included riebeckite ($(NaCa)_2(FeMn)_3Fe_2(SiAl)_8$), portlandite ($Ca(OH)_2$), calcium silicate ($Ca_2SiO_4$), hydrotalcite ($Mg_6Al_{12}CO_3(OH)_{16}\cdot 4H_2O$), and serandite ($Na(MnCa)_2Si_3O_8(OH)$) (Demeyer et al., 2001). Steenari and Lindqvist (1997) also report the components of grate fired boiler ashes include calcite, calcium hydroxide, calcium sulphate, and many other calcium, iron, magnesium, and aluminum compounds.

Biomass ash has a very high alkalinity, typically ranging from pH 9-13 (Demeyer et al., 2001; Steenari and Lindqvist, 1997; Steenari et al., 1999; Mahmood et al., 2002; Ozolincius et al., 2007a,b). One of the concerns associated with high pH ash is that it poses risk to ecological receptors (e.g. wildlife), and may create occupational hazards for individuals handling the material (Pitman, 2006). The calcium carbonate equivalence (CCE) has also been reported to be quite high as well, ranging from 50-90% CCE (Demeyer et al., 2001). Calcium carbonate equivalence is a measure of how close the neutralizing capacity of a material is compared to calcium carbonate (calcium carbonate has a CCE of 100%). High calcium carbonate equivalency and pH are the result of high combustion temperatures. At 1000°C oxides become dominant in ash, of which calcium oxide (lime) is the major component. Calcium oxide has a CCE greater than 100% resulting in the high CCE observed from analyzed biomass ashes (Demeyer et al., 2001).

Untreated ash, also termed loose ash, tends to pose several problems in regard to the utilization of biomass ash. The primary problem is that loose ash is very fine and subject to suspension in air (i.e. is dusty). Consequently, it is hard to handle, or spread evenly, and it poses health risks to operators (Pitman, 2006). Firstly, inhalation of alkaline ash poses an occupational risk. Secondly, loose ash can have negative effects on ground vegetation such as burning plant

tissue (Pitman, 2006; Mahmood et al., 2002). To overcome some of these problems, the untreated ash can be hardened. Two current techniques are used to produce crushed or granulated ash. Self-hardened ash is formed through moistening biomass ash to 30-60% (by mass) with water and allowing that to harden for several weeks. The self-hardened ash can then be crushed and sieved (into desired particle size ranges) for better application (Steenari and Lindqvist, 1997; Mahmood et al., 2002; Arvidsson et al., 2002; Jacobson and Gustafsson, 2001; Pitman, 2006; Steenari et al., 1999). Alternatively, granulated ash is produced by mixing ash with water and rolling the ash into balls of 4-20mm, which are then dried to <5% water content (Pitman, 2006).

Upon hardening, the mineralogical properties of loose ash change. In addition to an increase in carbonates, cement-based minerals such as portlandite ($Ca(OH)_2$) and ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$) are also formed (Steenari and Lindqvist, 1997). The formation of calcite, gypsum ($CaSO_4\cdot 2H_2O$), allophane ($Al_2O_3SiO_2\cdot 2.5H_2O$), and imogolite ($Al_2SiO_3(OH)_4$) were also detected for artificially weathered coal fly ash (Warren and Dudas, 1985). Elemental concentrations are often altered due to the hardening of ash. For example, hardened ash tends to have lower concentrations of calcium due to the formation of hydrates and carbonates (Pitman, 2006).

1.3 Use of Biomass Ash as Soil Amendment

Biomass ash has potential to act as a fertilizer and liming agent for agricultural and forest soils (Ozolincius et al., 2007b; Demeyer et al., 2001; McKendry, 2002b). Plants require N, P, K, Ca, Mg, and S in relatively large concentrations (macro-nutrients) and Fe, Mn, B, Zn, Cu, Cl, Co, Mo, and Ni in small concentrations (micro-nutrients) (Brady and Weil, 2002). Many of these elements are contained within ash except for nitrogen. Concentration of nitrogen is often low in woody biomass, and the nitrogen that is present is lost in the gas stream during combustion (Ozolincius et al., 2007b; Demeyer et al., 2001).

Chemical and biological assays (bio-assays) are often conducted for specific soil-ash combinations because nutrients present in biomass ash are not necessarily present in forms that are available to plants. For example, iron is one of the most abundant elements in soils, but under some conditions its bioavailability to plants can be limited. Similarly, phosphorus can convert to non-bioavailable forms upon reacting with soil components (McBride, 1994).

Studies that have shown benefits to tree growth using biomass ash as a soil amendment include Ozolincius et al. (2007a), Arvidsson and Lundkvist (2003), Park et al. (2005), and Jacobson and Gustafsson (2001). These studies observed increased growth in plant material treated with bottom ash. Furthermore, the addition of nitrogen to bottom ash treatments increased growth much more dramatically. Therefore, the addition of nitrogen fertilizer (commonly ammonium nitrate, NH_4NO_3) is often incorporated into soil with ash. Compared to non-fertilized stands, a combination of biomass ash and nitrogen encourages tree growth.

Agricultural crop growth also benefits from biomass ash. Increased crop growth has been shown for alfalfa and barley (Meyers and Kopecky, 1998), oats and beans (Krejsl and Scanlon, 1996), and Dallis grass-fescue (Muse and Mitchell, 1995). Patterson et al. (2004) report increased barley biomass and grain yield, and canola seed response to land application of wood ash in Alberta. These crop studies (including the tree growth studies) report using several tonnes of ash per hectare. The potential use of this much ash is desirable, as large amounts are generated from bioenergy plants.

Biomass ash has been utilized for other types of land applications. For instance, the remediation of highly acidic soils has also been accomplished through the addition of biomass ashes. Many tropical soils suffer from high acidity resulting in a high concentration of soluble aluminum and subsequent toxicity to plants. Application of wood ash has shown to improve

tropical soil quality by increasing pH and lowering the solubility of aluminum resulting in increased growth of rye grass as well (Nkana et al., 1998).

Many jurisdictions have regulations regarding the composition of ash materials and the quantity applied to land (Chapter 2, Table 2.0). In British Columbia, the land application regulations (Soil Amendment Code of Practice) state that 11 trace elements (As, Cd, Cr, Co, Cu, Pb, Hg, Mo, Ni, Se and Zn) must be monitored when applications of wood residue are applied; wood residue includes ash materials (SYLVIS, 2008) (Chapter 2, Table 2.0). Some biomass ashes contain polycyclic aromatic hydrocarbons (PAHs), dioxins and furans that originate from incomplete combustion (Sarenbo, 2009; Pitman 2006). For example, fly ash coming from the incomplete combustion of wood in boilers may contain as much as 1.4-7.2 mg kg^{-1} of PAHs in ash containing roughly 22% carbon (Sarenbo, 2009). Holmberg et al. (2000) stated that if ash carbon content is higher than 5%, then PAH analysis should be performed on ash samples. Several jurisdictions (e.g. Alberta, Sweden) have maximum allowable concentrations of PAHs in biomass ashes.

In Alberta the maximum allowable application rates are 15 tonnes ha^{-1} of wood ash to agricultural soils (Alberta Environment, 2002). In British Columbia, the application of ash materials cannot be performed if the site will become contaminated or exacerbate a contaminated site and the amendment must be applied in such a way to prevent any leachate or runoff from escaping the site (Environmental Management Act, 2007). In South Carolina, an application rate of up to 22 tonnes ha^{-1} of biomass ash is allowed on agricultural lands (Williams, 1997). This requires the application of biomass ash to be well away from wells, property lines, water ways, schools and hospitals (Williams, 1997).

One concern of ash application to land is the potential uptake of metals by plants and animals. One study has shown that plant uptake of non-nutrient metals is minimal in forest

berries, mushrooms, and plants (Moilanen et al., 2006). Many species studied by Moilanen et al. (2006) saw decreased metal accumulation over four years compared to the control data. Cadmium was the only metal showing increased accumulation in one species of mushroom, *Russula emetic* (Moilanen et al., 2006).

1.4 Leaching and Weathering Properties of Biomass Ash

An understanding of the weathering and subsequent leaching of metals from biomass ash is critical when considering ash for use as a soil amendment. Possible concerns when applying biomass ash to land is the potential contamination of water sources (surface or groundwater), and metal ions saturating soil and their leachability. Some of the methods that identify metal mobility through weathering and leaching include availability testing, serial batch extractions, column leaching, pH static leaching, and the toxicity characteristic leaching procedure (TCLP) (Steenari et al., 1999; Van der Sloot et al., 1996; Wahlstrom, 1996; USEPA Method 1311, 1992). Serial batch extractions or column studies are similar in end result and tend to be the leading weathering tests performed (Chimenos et al., 2000; Dudas, 1981; Gori et al., 2011; Holmberg, et al., 2000; Neupane et al., 2012; Steenari et al., 1999; Warren and Dudas, 1985).

Availability testing is used to determine the worst case scenario of metal leaching from inorganic wastes, providing insight into the total constituents involved in the entire leaching life of an inorganic waste (Wahlstron, 1996). Availability refers to the total loss of metals from an inorganic material due to leaching. This test is useful for landfill sites where inorganic wastes, such as biomass ash, may be disposed (Wahlstrom, 1996; Van der Sloot et al., 1996; Lewin 1996). The availability test is a leaching procedure involving the manual alteration of pH in two leaching cycles, providing a good technique for screening purposes of total metal mobility from inorganic wastes.

Metal mobility depends largely upon pH in aqueous solution. The pH static leaching procedure has been developed to determine the leachability of metals at specific pH values, creating a leaching profile of any analyzed element (Van der Sloot et al., 1996). The term "static" is used to indicate that pH was maintained at a specific value throughout the single extraction period.

Serial batch extraction is a leaching method involving the equilibration of a solid waste material with a leaching medium (typically water). After equilibration, the water is extracted and the same amount is added again for another round of equilibration. This can be done for several cycles to simulate long-term weathering. Normally, liquid to solid (L/S) ratios in batch extractions range from an L/S of 20-100 (Wahlstrom, 1996). Liquid to solid ratios refer to the amount of leaching medium used for the solid, by weight. Low L/S ratios more accurately represent rainwater saturation in soils, while high L/S ratios more accurately simulate contact with aqueous environments such as ponds or lakes (EPRI, 1991).

Column leaching is another form of weathering solid waste materials (similar outcome as the serial batch extractions) (Dudas, 1981; EPRI, 1991; Wahlstrom, 1996). In general, column studies involve packing the waste material of interest within a column and saturating the material with a steady flow of leaching medium that is run from one end of the column and collected on the opposite end.

Leaching can be studied by batch extractions or column studies; both have advantages and disadvantages (EPRI, 1991). The advantages of batch extractions include (i) good replication and reproducibility, (ii) control of master variables (e.g. pH, leaching medium, L/S ratio and ionic strength) are straightforward, (iii) direct evaluation of geochemical reactions can be studied and (iv) the thermodynamic and kinetic aspects of the geochemical reactions can be evaluated without hydrodynamic effects (EPRI, 1991). Hydrodynamic effect refers to the interaction between a

continuous flowing medium and particles within that medium. Batch extractions are useful weathering experiments that can provide information applicable to the field regardless of "water flow and other real-world complications related to heterogeneity in physical and chemical properties and in the structure of the porous medium" (EPRI, 1991, p.3-10). Limitations include the generation of colloidal materials due to agitation that can influence surface interaction results. In addition, multi-solute chromatographic effects are more difficult to evaluate (EPRI, 1991).

In contrast to batch extractions, column studies allow for the evaluation of geochemical properties in a physical environment and can be representative of a natural porous medium (EPRI, 1991). Furthermore, column studies allow for the evaluation of mass transport processes and how water flux and physical attributes of a porous medium affect the progress of geochemical reactions (EPRI 1991). The major advantage of column studies is their use to evaluate "how mass transport, porous media, and degree of saturation affect the rate and overall manifestation of geochemical reactions in flow through systems" (EPRI, 1991, p. 4-1). Limitations of column studies include high variability between studies and replicates; also its time consuming nature. The use of sieved or homogenized materials is not always directly applicable to the field because the structure of the natural porous media may have been destroyed (EPRI, 1991).

Several studies have employed the use of batch extractions and column studies to study the leaching phenomena of ash (Dudas, 1981; Holmberg et al., 2000; Steenari et al., 1999). Using batch extractions and a field study, Holmberg et al. (2000) discovered that granulated wood fly ash, containing 5% carbon and incorporated dolomite, contained some highly mobile elements (a rapid release of S, Cl, Na, and K was seen). Based on the results of their study, Holmberg et al. (2000) concluded their specific fly ash was not suitable for land application (i.e. nutrient recycling, even though elemental levels were within recommendations for ash recycling) without

the addition of dolomite, as the dolomite component (contained within the fly ash) was released very slowly.

Another study analyzed wood ashes from several grate-fired boilers through short-term sequential batch extractions (Steenari et al., 1999). Steenari et al. (1999) showed that granulated and lab hardened wood ash significantly reduced calcium leaching compared to untreated wood ash. The slow release of calcium was attributed to the formation of calcite. However, potassium release was not slowed by granulation but rather seemed to be controlled by particle size (Steenari et al., 1999). Due to the high pH induced by wood ash, the leaching of phosphorus and magnesium was low. Through thermodynamic modelling using EQ3NR (Wolery, 1983), Steenari et al. (1999) predicted that once a pH of 6 is achieved (after significant leaching), only quartz (SiO_2) and aluminum hydroxide ($Al(OH)_3$) would remain in the ash.

A long term study of fly ash from a coal fired power generation plant in Alberta, Canada, used columns to study the mobility of select metals (Dudas, 1981). Dudas (1981) showed that Ca, B, Sr, and V were preferentially leached. Much of the Al, Ba, Fe, K, Na, Mn, Pb, and Zn remained contained within the fly ash after leaching. Dudas (1981) concluded that coal fly ash leaching was dominated by the surface adsorbed inorganic salts. Once these salts were leached from the ash, solution concentrations of other elements were reported at relatively low levels (Dudas, 1981).

In a recent weathering experiment, a decrease in the solubility of Ba, Ca, and Zn was observed in hardened pellet ash compared to loose ash (Rehl et al., unpublished). In contrast an increased solubility of Cd, Mg, and P was observed in hardened ash compared to loose ash (Rehl et al., unpublished). The pH of treated ash did not vary considerably in lab-hardened ash treatments compared to those of non-hardened ash treatments (Rehl et al., unpublished).

The chemistry of mobilized constituents from ash materials will most likely be altered once coming into contact (i.e. react) with soil. In general, the mobility of ash constituents may be reduced due to various precipitation and sorption mechanisms (Pitman 2006). Pitman (2006) suggested that the leaching of soluble constituents from wood ash may be attenuated by the soil itself (relating to buffering capacity). Applications of wood ash on agricultural lands did not contaminate groundwater sources as the soil was able to attenuate many of the leached elements (Williams, 1997). Kahl et al. (1996) concluded that leached metals from soil receiving low ash application rates (6 tonnes ha^{-1}) were minimal. The buffering (i.e. attenuation) capacity of the soil was overloaded at heavier application rates (20 tonnes ha^{-1}) and a flux of Ca, Mg, Cl, and SO_4 was found within leachates along with a rise in pH (Kahl et al., 1996). In contrast, trace elements were still attenuated by soil or contained within ash at 20 tonnes ha^{-1} (Kahl et al., 1996).

The type of soil that ash is applied to, can also alter/influence the leachate composition resulting from weathered ash. Small increases in Ca, K, and SO_4 were observed in leachates when ash was applied to loamy sands in Maine, USA, as compared to soil controls; trace elemental concentrations were below detection limits (Williams et al., 1996). Increases in Ca, Mg, K, and SO_4 were observed in leachates from ash applied to drained bogs in Finland (Piirainen, 2001). Leachates coming from ash applications to hapotic podzol soils contained an increased concentration of Ca, Mg, Al, K, and SO_4 compared to that of soil controls (Saarsalmi et al., 2005). Finally, leachates taken from ash applied to podzolic soils over granite in Sweden contained increased concentrations of Ca and K over non-treated soils (Fransman and Nihlgard, 1995).

In summary, several methods are employed to study the weathering properties of ash. The most widely used methods include serial batch extractions and column leaching studies (Dudas, 1981; Holmberg et al., 2000; Neupane et al., 2012). Most research investigations on the

weathering properties or utilization of ash have been on ash derived from the combustion of coal. Not very many studies have investigated biomass ash (Steenari and Lindqvist, 1997; Steenari et al., 1999). Furthermore, ash interaction with soil has been mainly studied using coarse-textured soil (Fransman and Nihlgard, 1995; Piirainen, 2001; Saarsalmi et al., 2005). Not much is known about the interaction between fine-textured soil and ash.

1.5 Problem Formation and Overall Approach

It is apparent that biomass ash has the potential to be used as a fertilizer and amendment (i.e. liming agent) for agricultural and forest soils. Benefits include raising the pH and providing plant-essential elements. Biomass ashes tend to differ in their composition depending upon the biomass feedstock and the burning process used. Several gaps in our knowledge exist that need to be addressed.

First, (i) many studies focus on fly ash generated from coal combustion or co-generation combustion of biomass with coal and not on biomass ash (Dudas, 1981; Holmberg et al., 2000; Neupane et al., 2012); the influence of hardening is not widely studied either (Holmberg et al., 2000; Steenari et al., 1999). Although many studies focus on coal ash, leachate studies using coal ash could be insightful to determine if the major components leached are similar to that of biomass ash. The study of biomass ash (specifically bottom ash and lab-hardened bottom ash) would greatly add to this knowledge. Second, (ii) the long-term mobility of biomass ash components are relatively unknown as few studies have been done in this area (Dudas, 1981; Neupane et al., 2012). Short term studies have shown that many metals of concern are quite immobile due to the short term increase in pH (Holmberg et al., 2000; Steenari et al., 1999). However, it is unknown how elements may behave if, or when, ash components react for significant periods of time. Long-term leaching of biomass ash by serial batch extractions would further advance our knowledge. Third, (iii) the interaction between soil and ash has been studied

mainly on coarse soils (Fransman and Nihlgard, 1995; Piirainen, 2001; Saarsalmi et al., 2005). Scandinavian researchers have examined the responses of forest soils to ash addition for years (Fransman and Nihlgard, 1995; Piirainen, 2001; Saarsalmi et al., 2005). Studying the leachability of major and minor elements coming from a mix of fine-textured soils with biomass ash would add to our knowledge. Finally, (iv) leachability of constituents from biomass ash can be influenced by pH of the environment and is not widely studied (Dijkstra et al., 2006; Van der Sloot et al., 1996; Whalstrom, 1996). Manipulating the pH of the environment biomass ash is contained in would identify the characteristic pH profile of ash. This pH profile would help to understand how leaching changes.

1.6 Thesis Project Research Objectives

This project evaluated the potential for UNBC gasifier bottom ash to be used as a soil amendment. This was done by analyzing the long-term weathering of ash, hardened ash, the interaction of ash and soil, and how dictating the pH of the aqueous environment varied the leachability of major and minor elements in ash and hardened ash. Two research objectives were formulated.

Objective 1

To determine leachability of major and trace elements in both hardened and unhardened bottom ash, with and without the presence of a fine textured soil.

Objective 2

To determine the leachability of major and minor elements in both hardened and unhardened bottom ash in response to acidification.

2.0 Characterization and Long-Term Weathering of Bottom Ash

2.1 INTRODUCTION

The combustion of biomass in thermochemical processes, such as gasification, produces a by-product called biomass ash (McKendry, 2002a,b). This ash is divided into two categories, bottom ash and fly ash. Elements that become volatilized and carried away by the gas stream during biomass incineration are called fly ash once they condense and are caught by filters/precipitators. Bottom ash is usually dominated by the residual inorganic material leftover in the combustion/incineration chamber that did not volatilize (McKendry, 2002a,b). Bottom ash, which is generally produced in greater quantities than fly ash, is commonly landfilled. There is an interest in the utilization of biomass ash beyond landfilling, such as a component in cement (Rajamma et al., 2009; Wang et al., 2008), internal wall partitions (Leiva et al., 2009), and as a soil amendment (Arvidsson and Lundkvist, 2003; Demeyer et al., 2001; Ozolincius et al., 2007b; Park et al., 2005). The use of ash as soil amendment has gained most of the interest. Since many of the volatile, 'toxic', elements often end up in higher concentration in the fly ash, its use as a soil amendment is not as desirable as the use of bottom ash (Arvidsson and Lundkvist, 2003; Ozolincius et al., 2007a).

It is important to know the mineralogical and chemical composition of bottom ash if it is intended for use as a soil amendment. Bottom ash is a very fine alkaline material (pH 9-13). This alkalinity is mainly due to the presence of alkali and alkali earth metal oxides (Steenari et al., 1999). The major inorganic elements composing ash are Al, B, Ba, Ca, Fe, K, Mg, Mn, Na, P, Si, and Sr. The remainder of the ash is comprised mainly of As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Se, and Zn (Gori et al., 2011; Steenari et al., 1999; Rehl et al., unpublished).

Application of ash to soil returns nutrients to soil and can raise the pH of acidic soils (Nkana et al., 1998). However, excessive rates of application of ash to soil could raise the pH to

unacceptable levels and overload soil with trace elements of environmental concern. The mobility of added trace elements may also pose risks. Application of loose ash to soil may result in a rapid dissolution of hydroxides and carbonates from ash (Holmberg et al., 2000; Steenari et al., 1999). A solution to limiting this rapid release is through the hardening of bottom ash prior to use. Hardening is accomplished by the addition of water and allowing the ash to react to form new minerals, such as gypsum, portlandite, ettringite, calcite, allophane, imogolite, and riebeckite (Dudas, 1981; Steenari and Lindqvist, 1997). These mineral formations reduce the solubility of ash and also the leachability of many elements (Steenari et al., 1999).

Simulated weathering of bottom ash and the resulting leachates are not widely studied. The properties and elemental mobility of ash have been studied on coal fly ashes (Dudas, 1981; Holmberg et al., 2000; Neupane et al., 2012) and grate-fired boiler ashes (Steenari et al., 1999). Many studies focus on fly ashes and do not examine long-term elemental mobility. Furthermore, the short- and long-term mobility of ash components are not fully understood when ash is mixed with soil.

Suitable methods for studying the long-term weathering of bottom ash include serial batch extractions and column leaching studies. Even though column studies may be more relevant to the field, the variability in results between experiments (and replicates) makes them unfavourable when studying geochemistry (EPRI, 1991). Generally, serial batch extractions have greater reproducibility and are therefore suggested as the standard leaching procedure for waste materials (EPRI, 1991).

Trace elements have leached in minimal amount from ash mixed with coarse-textured soils (Fransman and Nihlgard, 1995; Kahl et al., 1996; Piirainen, 2001; Saarsalmi et al., 2005). Few studies have examined elemental mobility when a fine-textured soil is mixed with ash. In general, it is expected that soil will attenuate the ability for many elements to be leached from ash

through precipitation and adsorption reactions (Fransman and Nihlgard, 1995; Piirainen, 2001; Pitman, 2006; Saarsalmi et al., 2005). However, this assumption may not hold for fine-textured soil, or for all ashes. Using a long-term serial batch extraction to simulate bottom ash weathering, this study will determine the leachability of major and trace elements in both hardened and unhardened bottom ash, with and without the presence of a fine-textured soil.

2.2 METHODOLOGY

2.2.1 Collection of Bottom Ash from UNBC Gasifier

Bottom ash from the UNBC gasifier was collected at a sampling grate port located at the beginning of the conveyer belt that transported bottom ash away to a collection bin. The feedstock for this gasifier was a mix of hog fuel, pine, and balsam fir waste (ranging from bark to sawdust). Bottom ash samples were collected 6 times over two months (June 23, June 27, July 6, July 7, July 11, July 12; all of 2011). This study focused on the bottom ash; however, some characterization was conducted on fly ash and fly-bottom ash mixes (reported in Appendix A1)

2.2.2 Preparation of Collected Bottom Ash

Bottom ash samples were thoroughly mixed together and sieved through a 2mm screen to remove clinker and any rocks that may have originated with the hog fuel. Any char that was removed through sieving was re-collected and re-mixed with bottom ash. In this study, the loose, unhardened bottom ash is henceforth referred to as bottom ash.

2.2.3 Preparation of Hardened Bottom Ash

Sieved bottom ash was wetted with double deionized water (40% w/w) and placed on an inert surface in an indoor environment. The wetted bottom ash was formed into flat sheets approximately 2cm in thickness. Sheets were left to harden for a total of four weeks. Once hardened, the bottom ash was crushed to produce granules <10mm and was then sieved through a 2mm screen. Only granules <10mm and >2mm were used in the study. Granules <2mm in size

were subjected to elemental analysis and were found to have similar composition as the larger granules (Appendix A1).

2.2.4 Collection and Preparation of Soil

The soil sample was collected (0-30cm depth) on May 13, 2010 from an agricultural field located approximately 10km NW of Prince George, British Columbia (N54° 04' 20.156" and W122° 48' 01.796"); the property had been cleared of forest approximately 7 years prior to soil collection. The soil sample collected was from an Ap horizon, a mixture of A and B horizon materials with some organic material from the original forest organic horizons. Once collected, the soil was air-dried on plastic sheets, sieved through a 4mm screen, homogenized, and stored in a sealed container at 4°C until needed.

2.2.5 Characterization of Ash and Soil Samples

2.2.5.1 Electrical Conductivity (EC) and pH

Electrical conductivity (EC) testing was performed by obtaining air-dry equivalent amounts of sample to make a liquid/solid mass ratio (L/S) of 5, using deionized water, according to methods performed by Haglund (2008). The analysis was performed in quadruplicate. Samples were transferred into Nalgene centrifuge tubes and an appropriate amount of double deionized water was added. Samples were capped and shaken on an orbital table shaker (Barnstead Lab-Line Model 4633) at 280rpm for 1hr. After agitation, the samples were vacuum filtered (Whatman No. 41) and EC was promptly obtained using a calibrated YSI Conductivity Instrument.

The pH of loose bottom ash, hardened bottom ash, and soil were determined according to Kalra and Maynard (1991). An amount of 25.0g (to the nearest 0.001g) of air dry sample was mixed with 50.0mL of double deionized water and stirred every 5min for 30min. After stirring

the samples were allowed to settle for 30min; pH readings were promptly taken using a calibrated Thermo Orion 420A+ meter (buffer solutions containing pH 4, 7, and 10 were used).

2.2.5.2 Gravimetric Moisture Content

Moisture content of loose bottom ash, hardened bottom ash, and soil was determined according to Kalra and Maynard (1991). Samples (four replicates) were weighed out to approximately 10g (measured to the nearest 0.01g) in aluminum weigh boats and placed into a drying oven at 105°C for 24 hours. Gravimetric moisture content was determined by calculating the mass loss of water relative to the oven-dry (OD) weight of the solids (i.e. g H_2O g^{-1} OD solids; or g H_2O $100g^{-1}$ OD solids).

2.2.5.3 Effective Cation Exchange Capacity (CEC) for Soil

Effective cation exchange capacity (CEC) for soil was determined according to Hendershot and Duquette (1986). Briefly, effective CEC is the sum of exchangeable cations (Ca, Mg, K, Na, Al, Fe, and Mn) contained within soil. A solution of $BaCl_2$ is used to displace the cations Ca, Mg, K, Na, Al, Fe, and Mn contained within soil, which are then measured in the filtered supernatant by atomic absorption spectroscopy. In a 50mL centrifuge tube, 30.0mL of 0.1M $BaCl_2$ was added to 1.5g of air-dry soil (measured to the nearest 0.001g) and shaken on an end-over-end shaker (15rpm) for 2 hours. The mixture was centrifuged (15min at 700 times gravity) and vacuum filtered with a Whatman No. 41 filter paper. The supernatant was then analyzed by an atomic absorption spectrometer for Ca, Mg, K, Na, Al, Fe, and Mn. Effective CEC was then determined by summing the exchangeable cations, which were determined according to the equations found in Hendershot and Duquette (1986).

2.2.5.4 Particle-Size Analysis of Soil

Particle-size analysis of soil was performed according to Kalra and Maynard (1991). Briefly, the soil was separated into different fraction sizes corresponding to fractions of sand, silt,

and clay as determined by the sedimentation principle based on Stoke's law. Calgon solution (50.0mL) and water (400.0mL) were stirred with soil (50g, measured to the nearest 0.001g) for 15 minutes, and then transferred to a sedimentation cylinder. The suspension was made up to the 1L mark, covered, and allowed to stand overnight; a blank consisting of calgon was also made. The suspension was stirred vigorously using the supplied cylinder plunger and a hydrometer reading was taken 40 seconds after the plunger was removed. Temperature of the suspension was then recorded at a 5cm depth. Hydrometer and temperature readings were taken again at the end of two hours (correction factor of +/- 0.36 graduations to the hydrometer for every +/- 1°C). Hydrometer readings were further adjusted by subtracting the blank readings. Sand, silt, and clay fractions were calculated as a percent of the original soil amount according to these next equations: silt + clay (%) = (corrected hydrometer reading (at 40s)/sample weight)*100, and clay (%) = (corrected hydrometer reading (at 2 hours)/ sample weight)*100, and sand (%) = 100 – (Silt% + Clay%).

2.2.5.5 Calcium Carbonate Equivalency (CCE)

Calcium carbonate equivalency was determined according to Goh and Mermut (2008). Briefly, a standard curve of known milligrams of calcium carbonate (in logarithm) against the pH of neutralized calcium carbonate was used to compare unknown samples of ash and soil to calcium carbonate. Standards of calcium carbonate ($CaCO_3$) were weighed from 5mg to 500mg (measured to the nearest 0.001g) and transferred to conical centrifuge tubes. Acetic acid (25.0mL, 0.4M) was then added to each conical tube to neutralize the calcium carbonate. All the samples were quickly hand shaken, vented, and then placed overnight on a horizontal table shaker on low. Once the samples had been shaken they were vented again and given a final degassing for 5 minutes using a sonicator (Branson 1510) and centrifuged (HERMLE Z328) at 1500rpm for 15 minutes. The pH was then promptly taken and used to create the standard curve according to

equations used by Goh and Mermut (2008). Analysis of ash and soil samples would then be analyzed using the same procedure but with 400mg samples (measured to the nearest 0.001g) and comparing the standard curve for their equivalence to calcium carbonate.

2.2.5.6 Elemental and Total C/N/S Analysis

Samples of the solid phase materials used, including TILL 3 standard, were sent to Victoria, BC, to be analyzed for total elemental content by the BC Ministry of Environment. Determination of elemental content was done using an ICP-OES (Teledyne/Leeman Prodigy) following EPA digestion Methods 3051A and 3052 (performed by BC Ministry of Environment) for Al, Ba, Ca, Fe, K, Mg, Na, P, S, As, B, Bi, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Se, Sr, Zn, Ag, Be, Bi, Li, Sb, Sn, Ti, Tl, U, V, W, Y, and Zr; the BC Ministry of Environment also ran reagent blanks alongside the elemental analysis for QA/QC. Two digestion methods, HCl/HNO_3 (EPA Method 3051A) and $HNO_3/HF/H_2BO_3$ (EPA Method 3052), were performed to determine if there was a difference in the completeness of the digestion for the requested elements. A TILL 3 standard was included with the solid samples, for QA/QC purposes (CCRMP, 1995). Many of the elements analyzed were below the allowable 15% relative percent difference (Clark, 2003) of the TILL 3 Certificate of Analysis indicating thorough dissolution and analysis of the solid materials (Appendix A1, Tables A1.12 and A1.13). Total carbon, organic C, inorganic C (determined by difference), and total nitrogen were determined by dry combustion using a Fisons (Carlo Erba) NA-1500 CHS analyzer (Skjemstad and Baldock, 2008). In addition to ICP determination of sulphur, total sulphur was also determined by dry combustion, using a Leco Truspec CNS analyzer (Leco Corporation, 2008).

2.2.6 Serial Batch Extraction (Long-Term Weathering)

The methods for long-term weathering were adapted from Steenari et al. (1999). Four replicates of bottom ash (BA), hardened bottom ash (HBA), soil, 5%w/w BA with soil (5%BA),

and 5%w/w HBA (5% HBA) with soil were prepared in separate 250mL Nalgene centrifuge tubes (mass ratios of ash and soil done on an equivalent dry weight basis). Reagent grade (i.e. double deionized water) water was used throughout the entire experiment (Clark, 2003); this was water that first went through a reverse osmosis process, and was then passed through a MilliQ machine to achieve an electrical resistance of 18.2MΩ. Double deionized water was then added at an L/S 20 to each sample (e.g. 7.000g of sample required 140.0mL double deionized water). Samples were capped and shaken on an orbital table shaker (Barnstead Lab-Line Model 4633) for 23 hours at 220rpm. After 23 hours the samples were centrifuged at 24000xg (BECKMAN COULTER Avanti J-E Centrifuge). Vacuum filtration was done using Nalgene filter-ware and 0.45μm filter papers (Whatman No. 41). Double deionized water was then again added to the original treatments at an L/S ratio of 20 and placed back on the orbital shaker for another 23 hours. Blanks were run simultaneously with the serial batch extraction for QA/QC, and revealed only trace amounts of the analyzed elements to be present within the aqueous phase of the blanks (Appendix A1, Table A1.11). This cycle was repeated a total of 20 times. The aqueous extracts were then transferred to labelled conical tubes for analysis. Electrical conductivity (EC) (YSI Conductivity Instrument), oxidation reduction potential (ORP) (Thermo ORION 3 STAR pH Benchtop Meter) and pH (Thermo Orion 420A+ Meter) were promptly obtained. Elemental analysis was performed by the UNBC Central Equipment Laboratory (CEL) using ICP-MS (Agilent Technologies 7500 Series ICP-MS) for Al, Ba, Ca, Fe, K, Mg, Na, P, Si, As, B, Bi, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Se, Sr, Zn, Ag, Be, Bi, Li, Sb, Sn, Ti, Tl, U, V, W, Y and Zr; the analysis encompassed all speciations for each element as a total, unless otherwise stated. For days 1, 10 and 20, including the elemental analysis, a full anion scan (Br^-, Cl^-, F^-, NO_3^-, NO_2^-, PO_4^{3-} and SO_4^{2-}) was performed using ion-chromatography (Waters 1525 Binary HPLC Pump equipped with a Metrohm 833 Suppressor and Waters 432 Conductivity Detector) from modified

Metrohm IC Application Note No. S-257, and an alkalinity scan by the BC Ministry of Environment (Victoria, BC).

2.2.7 Statistical Analysis of Serial Batch Extraction

Analysis of variance (ANOVA) was performed on data generated from the serial batch extraction using the software package CoStat Ver. 6.3111. A one-way completely randomized ANOVA test was performed on data from each of day 1, 10, and 20, followed by (if ANOVA was significant) Tukey's Honest Significant Difference (HSD) method to compare treatment means. Details of statistical results are presented in Appendix A3. Tables and figures present means and standard deviations.

2.2.8 MINTEQ Modelling

Elemental data, anion data, pH, oxidation reduction potential, and temperature obtained from the different analyses performed on the serial batch extracts were input into MINTEQ modelling to produce a saturation index for minerals (Tables 2.6 to 2.10). Calculated results were obtained from data that contained <20% mass charge imbalance according to Visual MINTEQ v3.0; mass charge imbalance refers to the sum of the cations and anions entered into MINTEQ modelling. Elements that were undetected were entered at half the value of their detection limit. Saturation index (SI) is an index value that is used to show whether a particular mineral will dissolve or precipitate in an aqueous solution. SI is calculated by comparing the chemical activities, ion activity product (IAP) and solubility product (K_s), of dissolved ions for a desired mineral; $SI = \log(IAP) - \log(K_s)$. A saturation index <0 indicates undersaturation of a mineral, meaning that if the solid mineral were in contact with the solution, the solid mineral would dissolve. Whereas a value >0 indicates oversaturation of a mineral, meaning that at the observed ion concentrations, a given mineral would precipitate from solution. A saturation index of 0

indicates that a given mineral in solution would neither precipitate from solution nor dissolve into solution (Meima et al., 2002).

2.3 RESULTS

2.3.1 Initial Properties of Ash and Soil

The elemental composition of the un-weathered ash and soil were determined by ICP-OES following HCl/HNO_3 digestion (Table 2.0). The major constituents of (herein defined as being greater than 1000mg kg^{-1} in the solid phase) bottom ash and hardened bottom ash were found to be Al, Ca, Fe, K, Mg, Mn, Na, P, and S (Table 2.0). The trace elements As, B, Ba, Co, Cr, Cu, Mo, Ni, Sr and Zn made up the remainder of the bottom ash and hardened bottom ash solid phases (Table 2.0). Elements found to be below the detection limits of the ICP-OES were Ag, Be, Bi, Cd, Hg, Pb, Sb, Se, Tl, U, and Y (Table 2.0). Moisture content for bottom and hardened bottom ash were very low (0.196% and 0.646% respectively); total carbon content was low as well (2.95% and 3.03% respectively) (Table 2.0). The soil used in this study was a silty-clay loam (10.6% sand, 53.5% silt and 35.9% clay) with a cation exchange capacity of 11.8 cmol+ kg^{-1} ($\pm$0.1cmol+ kg^{-1}).

Ash is composed of a number of metallic elements, some of which were measured in this study (Table 2.0), as well as oxygen, hydrogen, carbon and other non-metallic elements that compose silicates, oxides, hydroxides, carbonates, and sulphate minerals (Kirby and Rimstidt, 1993; Meima and Comans, 1999; Meima et al., 2002; Steenari and Lindqvist, 1997). A mass balance is only possible if one considers these other (non-measured) components, in addition to the major inorganic elements reported in this study (Table 2.0).

Bottom ash, hardened bottom ash, and soil were digested using two methods (HCl/HNO_3 and $HNO_3/HF/H_2BO_3$; data in Appendix A1). The elements Ag, As, B, Ba, Be, Bi, Cd, Hg, Pb, Sb, Tl, U, and Y were more accurately determined by ICP-OES using the HCl/HNO_3 digestion method. ICP-OES analysis of ash following $HNO_3/HF/H_2BO_3$ digestion revealed slightly better dissolution for Al, Cr, Cu, Fe, K, Mg, Na, S, Sn, Sr, Ti, V, Zn, and W. The elements Ca, Co, Li,

Mn, Mo, Ni, P, and Zr showed no discernible measured difference by ICP-OES from either digestion method. These determinations were based on which method gave higher readings. Since elemental analysis of ashes found in literature are primarily reported using HCl/HNO_3 digestion procedures, this study will also focus on data obtained from ICP-OES following HCl/HNO_3 digestion. However, ICP-OES analysis of ash following $HNO_3/HF/H_2BO_3$ digestion was also reported in Appendix A1.

*Table 2.0 – Initial (solid phase) properties of bottom ash (BA), hardened bottom ash (HBA), and soil control prior to serial batch extraction and maximum allowable limits (except for *, which designates minimum allowable limit) for several monitored elements by BC Soil Amendment Code of Practice (SACoP), Alberta, Denmark, Finland and Sweden**.*

Parameter	BA		HBA		Soil Control		SACoP	Alberta	Denmark	Finland	Finland	Sweden
	Mean	*SD*	*Mean*	*SD*	*Mean*	*SD*			*Agr./For.*	*Agr.*	*For.*	*For.*
pH	12.28	0.02	11.77	0.02	5.19	0.01						
EC ($\mu S\ cm^{-1}$)	9890	60	3093	106	73.0	4.0						
Moisture Content (%)	0.196	0.004	0.646	0.042	9.81	0.92						
Total N (%)	0.0143	0.001	0.013	0.001	0.131	0.003						
Total S (%)	0.032	0.019	0.0267	0.0078	0.0128	0.0004						
Total C (%) (inorganic)	1.34	0.039	1.57	0.13	<0.05	n/a						
Total C (%) (organic)	1.60	0.099	1.47	0.274	2.03	0.06						
Total C (%)	2.95	0.091	3.03	0.24	2.03	0.06						
CCE (%)	30.5	2.0	29.2	2.3	0.467	0.010						
Elemental Composition via ICP-OES following HCl/HNO_3 digestion												
Ag (ppm)	<1.0	n/a	<1.0	n/a	<1.0	n/a						
Al (%)	1.70	0.09	1.65	0.04	2.66	0.15						
As (ppm)	5.98	0.25	6.94	1.48	6.81	0.35	75			25	30	30
B (ppm)	140	4	120	7	4.44	1.28		43				800
Ba (ppm)	1340	15	1255	57	265	15						
Be (ppm)	<1.0	n/a	<1.0	n/a	<1.0	n/a						
Bi (ppm)	<1.0	n/a	<1.0	n/a	<1.0	n/a						
Ca (%)	11.2	0.3	9.98	0.36	0.506	0.009				8*	6*	12.5*
Cd (ppm)	<1.0	n/a	<1.0	n/a	<1.0	n/a	20	46	15	1.5	17.5	30
Co (ppm)	18.2	2.2	16.2	1.1	21.7	1.3	150					
Cr (ppm)	37.0	6.7	36.3	3.6	46.7	1.4	1060		100	300	300	100

Table 2.0 – Initial (solid phase) properties of bottom ash (BA), hardened bottom ash (HBA), and soil control prior to serial batch extraction and maximum allowable limits (continued).

Parameter	BA		HBA		Soil Control		SACoP	Alberta	Denmark	Finland	Finland	Sweden
	Mean	*SD*	*Mean*	*SD*	*Mean*	*SD*			*Agr./For.*		*Mean*	*SD*
Cu (ppm)	47.8	1.8	44.2	2.0	17.4	0.2				600	700	400
Fe (%)	1.54	0.08	1.63	0.11	2.92	0.02						
Hg (ppm)	<2.0	n/a	<2.0	n/a	<2.0	n/a	5		0.8	1	1	3
K (%)	1.97	0.09	1.94	0.08	0.418	0.050				(K+P) 2*	(K+P) 1*	3*
Li (ppm)	11.3	0.8	11.9	0.8	25.0	1.0						
Mg (%)	1.34	0.04	1.25	0.04	0.695	0.003						1.5
Mn (%)	0.658	0.020	0.580	0.024	0.107	0.003						
Mo (ppm)	5.85	0.22	5.77	0.27	<1.0	n/a	20					
Na (%)	0.425	0.043	0.430	0.026	0.040	0.006						
Ni (ppm)	61.0	6.2	55.8	2.4	28.0	0.5	180		30	100	150	70
P (%)	0.566	0.014	0.502	0.023	0.116	0.002				(K+P) 2*	(K+P) 1*	0.7*
Pb (ppm)	<2.0	n/a	<2.0	n/a	3.88	0.54	500		120	100	150	300
S (%)	0.125	0.004	0.104	0.007	0.012	0.0004						
Se (ppm)	<10	n/a	<10	n/a	<10	n/a	14					
Sb (ppm)	<4.0	n/a	<4.0	n/a	<4.0	n/a						
Sn (ppm)	2.20	0.39	1.36	0.37	<1.0	n/a						
Sr (ppm)	435	7	403	17	67.4	2.2						
Ti (ppm)	843	120	938	58	1546	17						
Tl (ppm)	<2.0	n/a	<2.0	n/a	<2.0	n/a						
U (ppm)	<20	n/a	<20	n/a	<20	n/a						
V (ppm)	43.3	2.4	47.1	1.9	99.4	2.4						70
Y (ppm)	<2.0	n/a	<2.0	n/a	<2.0	n/a						
Zn (ppm)	148	53	93.7	4.8	144	3	1850	5500		1500	4500	7000 (500*)
Zr (ppm)	14.5	0.6	14.9	1.2	12.1	3.9						

**Minimum allowable*

***Agriculture (Agr.), Forestry (For.)*

Some elements were found in greater or lower concentrations in bottom ash and hardened bottom ash than the soil control. Elemental enrichment factors (EF = concentration of elemental in ash ÷ concentrations in soil) are presented in Table 2.1. Values > 1 indicate that ash contained a higher concentration than soil of a specific element, whereas values < 1 indicate that the soil sample contained a higher concentration of a specific element than ash. Elements found to be enriched in soil were total N, Al, Cr, Li, Pb, Ti, and V. Elements found to be enriched in both ashes compared to soil were total C, B, Ba, Ca, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, S, Sn, and Sr. Elements that were found to be approximately the same in both ash and soil (or at very low concentration in both) were Ag, As, Be, Bi, Cd, Co, Hg, Sb, Tl, U, Y, and Zr. Zinc was depleted in hardened bottom ash relative to soil, but was found to be the same for untreated bottom ash and soil.

Table 2.1 – Relative enrichment of elements contained within bottom ash and hardened bottom ash relative to soil control.

Parameter	BA / Soil	HBA / Soil
Total N	0.11	0.10
Total S	2.53	2.08
Total C (organic)	0.79	0.72
Total C	1.46	1.50
Elemental Content		
Al	0.64	0.62
As	0.88	1.02
B	31.5	27.0
Ba	5.06	4.73
Ca	22.2	19.7
Co	0.84	0.74
Cr	0.79	0.78
Cu	2.74	2.54
Fe	0.53	0.56
K	4.72	4.64
Li	0.45	0.48
Mg	1.93	1.80
Mn	6.13	5.40
Na	10.7	10.8
Ni	2.18	2.00
P	4.87	4.32
S	10.3	8.59
Sr	6.46	5.98
Ti	0.55	0.61
V	0.44	0.47
Zn	1.03	0.65
Zr	1.21	1.24

**EF could not be calculated for Ag, Be, Bi, Cd, Hg, Mo, Pb, Sb, Se, Sn, Tl, U, Y and Total C (inorganic) since data fell below analytical detection limits*

2.3.2 Serial Batch Extraction

2.3.2.1 Changes in Solid Phase Composition During Long-Term Weathering

The percent mass loss of single elements leached from their respective starting material was calculated by determining the mass of a single element contained within each extraction solution, summing these over the 20 extractions, and expressing the results relative to the initial mass of an element contained within the solid phase of the starting materials. These results provide an indication of the potential mobility of specific elements during weathering. The percent mass loss of each element from bottom ash, hardened bottom ash, soil control, and ash-soil mixes ranged from $\leq$ 1% to $\geq$ 80% (Tables 2.2 to 2.4).

Mass losses >10% for individual elements contained in bottom ash and hardened bottom ash were found for B, Ba, Ca, Cr, K, Mo, Na, S, and Sr (Table 2.2 to 2.4). Mass losses >10% for individual elements from soil control were found for B and S (Table 2.2 to 2.4). Mass losses >10% for individual elements from bottom ash mixed with soil were B and S (Table 2.2 to 2.4). Mass losses >10% for individual elements from hardened bottom ash mixed with soil were B, Ca, Mo, Na, S, Sn, and Sr (Table 2.2 to 2.4).

Table 2.2 – Mass loss (%) of individual elements over the 20-cycle serial batch extraction for bottom ash, hardened bottom ash, soil control, 5% bottom ash, and 5% hardened bottom ash, relative to initial masses present in the solid phase within each experimental unit (determined via ICP-OES following HNO_3/HCl digestion).

Parameter (%)	BA	HBA	Soil	5%BA	5%HBA
	Mean	*Mean*	*Mean*	*Mean*	*Mean*
Al	6.88	3.59	0.39	0.83	0.73
As	3.14	2.47	1.56	5.37	5.03
B	54.63	57.57	11.23	28.73	62.72
Ba	15.17	11.07	0.57	1.00	3.66
Ca	27.7	13.3	1.68	17.3	23.2
Co	0.01	0.01	0.87	0.76	0.81
Cr	10.71	10.86	0.38	0.62	1.05
Cu	3.60	0.28	1.26	2.47	2.06
Fe	0.0067	0.0034	0.73	0.59	0.63
K	19.06	22.12	2.16	5.42	8.11
Li	1.70	2.05	0.12	0.09	0.11
Mg	0.44	0.84	0.94	3.12	4.48
Mn	0.005	0.004	1.66	1.51	1.57
Mo	53.98	44.55	n/a	n/a	132.38
Na	13.06	14.54	8.18	8.98	16.07
Ni	0.06	0.04	0.60	0.80	0.73
P	0.43	0.48	2.06	6.53	6.16
Pb	n/a	n/a	2.86	n/a	n/a
S**	27.0	29.8	87.4	61.1	67.0
Sn	1.02	1.22	n/a	n/a	12.64
Sr	23.70	14.38	1.25	7.70	11.20
Ti	0.0052	0.0049	0.23	0.22	0.22
V	8.07	6.50	0.55	1.01	1.02
Zn	0.31	0.29	0.60	0.54	0.56
Zr	n/a	n/a	0.39	0.52	0.49

**n/a refers to below detection limit*

***Sulphur mass loss (%) based only on solid phase data (final sulphur content – initial sulphur content)*

****Ag, Be, Bi, Cd, Hg, Pb, Sb, Tl, U, and Y were undetected*

Table 2.3 – Percent loss of elements over 20-cycle serial batch extraction relative to initial contents in solid phase as determined by ICP-OES following HNO_3/HCl digestion.

	BA	HBA	Soil	5%BA	5%HBA
<1%	Co, Fe, Mg, Mn, Ni, P, Ti, Zn	Co, Cu, Fe, Mn, Ni, P, Ti, Zn	Al, Ba, Co, Cr, Fe, Li, Mg, Ni, Ti, V, Zn, Zr	Al, Co, Cr, Fe, Li, Ni, Ti, Zn, Zr	Al, Co, Fe, Li, Ni, Ti, Zn, Zr
1% to 10%	Al, As, Cr, Cu, Li, Sn, V	Al, As, Cr, Li, Mg, Sn, V	As, Ca, Cu, K, Mn, Na, P, Pb, Sr	As, Ba, Cu, K, Mg, Mn, Na, P, Sr, V	As, Ba, Cr, Cu, K, Mg, Mn, P, V
11% to 20%	Ba, K, Na	Ca, Ba, Na, Sr	B	Ca	Na, Sn, Sr
21% to 30%	Ca, S, Sr	K, S	n/a	B	Ca
40% to 50%	n/a	Mo	n/a	n/a	n/a
50% to 70%	B, Mo	B	n/a	S	B, S
>80%	n/a	n/a	S	n/a	Mo
Undetected	Ag, Be, Bi, Cd, Hg, Pb, Sb, Se, Tl, U, Y, Zr	Ag, Be, Bi, Cd, Hg, Pb, Sb, Se, Tl, U, Y, Zr	Ag, Be, Bi, Cd, Hg, Mo, Sb, Se, Sn, Tl, U, Y	Ag, Be, Bi, Cd, Hg, Mo, Pb, Sb, Se, Sn, Tl, U, Y	Ag, Be, Bi, Cd, Hg, Pb, Sb, Se, Tl, U, Y

**Sulphur percent loss was based on solid phase data*

Table 2.4 – Percent loss of elements over 20-cycle serial batch extraction relative to initial contents in solid phase as determined by ICP-OES following HNO_3/HF/H_2BO_3 digestion.

	BA	HBA	Soil	5%BA	5%HBA
<1%	Co, Fe, Mg, Mn, Ni, P, Sn, Ti, Zn	Co, Cu, Fe, Mg, Mn, Ni, P, Sn, Ti, Zn	Al, Ba, Ca, Co, Cr, Cu, Fe, K, Li, Mg, Na, Ni, Sr, Ti, V, W, Zn, Zr	Al, Ba, Co, Cr, Fe, Li, Na, Ni, Ti, V, Zn, Zr	Al, Co, Cr, Fe, Li, Na, Ni, Ti, V, Zn, Zr
1% to 10%	Al, Ba, Cr, Cu, K, Li, Na, V, W	Al, Ba, Ca, Cr, Li, Na, V, W	Mn, P	Cu, K, Mg, Mn, P, Sr, W	Ba, Cu, K, Mg, Mn, P, Sr, W
11% to 25%	Ca, Sr	K, S, Sr	n/a	Ca	Ca
35% to 50%	S	Mo	n/a	n/a	n/a
50% to 70%	Mo	n/a	n/a	n/a	S
Undetected	Ag, As, Be, Bi, Cd, Hg, Pb, Se, Tl, U, Y, Zr	Ag, As, Be, Bi, Cd, Hg, Pb, Sb, Se, Tl, U, Y, Zr	Ag, As, Be, Bi, Cd, Hg, Mo, Pb, Sb, Se, Sn, Tl, U, Y	Ag, As, Be, Bi, Cd, Hg, Mo, Pb, Sb, Se, Sn, Tl, U, Y	Ag, As, Be, Bi, Cd, Hg, Mo, Pb, Sb, Se, Sn, Tl, U, Y

* *Sulphur percent loss was based on solid phase data*

***Sulphur percent loss for soil control and 5%BA were 145% and 89.1% respectively*

Although Table 2.3 and 2.4 revealed that there was a loss of elements from the ash, soil control, and ash-soil mixtures, the ash itself was relatively insoluble. This was revealed by comparing the initial mass of ash in the serial batch extraction to the mass that followed after the serial batch extraction was complete. The mass recoveries at the end of the study were 99.11% ± 0.05%, 99.34% ± 0.16%, 97.28% ± 0.03%, 97.41% ± 0.03% and 97.43% ± 0.05% for bottom ash, hardened bottom ash, soil, 5% bottom ash, and 5% hardened bottom ash respectively. Some loss can be attributed to trace amounts left on the filter paper.

2.3.2.2 Aqueous Phase Chemistry During Long-Term Weathering

Extracts from bottom ash and hardened bottom ash treatments showed higher pH values than soil and the ash-soil mix extracts (Figure 2.0). Overall, observed pH values declined with time for all treatments except for soil (Figure 2.0).

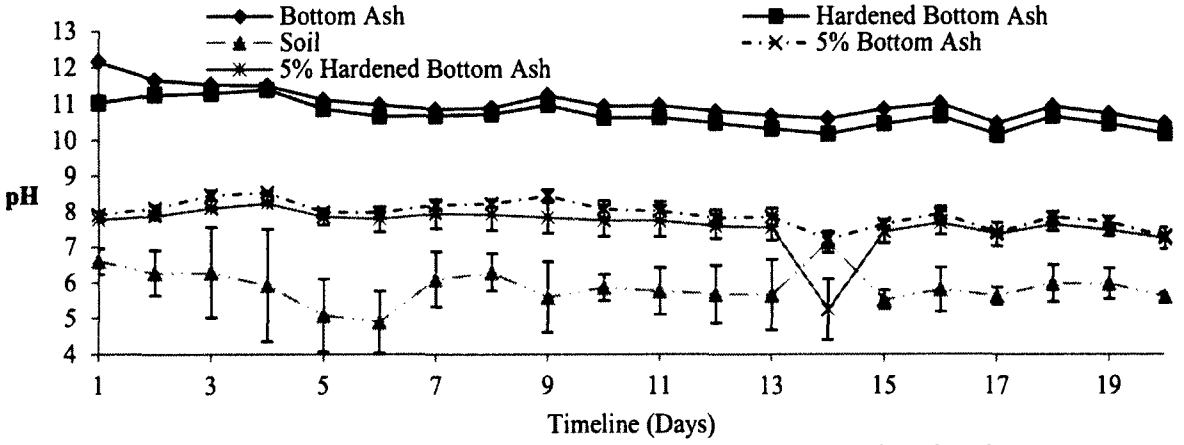

Figure 2.0 - Serial batch extraction of bottom ash, hardened bottom ash, soil, and 5% bottom and hardened bottom ash mixed with soil depicting pH values (with standard deviation error bars) over the twenty day timeline; n=4.

The electrical conductivity in aqueous extracts was higher from bottom ash and hardened bottom ash treatments than soil and ash-soil mix treatments (Figure 2.1). The high initial electrical conductivity in the aqueous extracts from bottom ash declined rapidly over time. Whereas, the electrical conductivity of aqueous extracts from hardened bottom ash were below that of bottom ash, and were relatively unchanged as time progressed (Figure 2.1). Electrical conductivity of the aqueous extracts from ash-soil mixes neared the measurements taken from soil control extract near the end of the serial batch extraction (Figure 2.1).

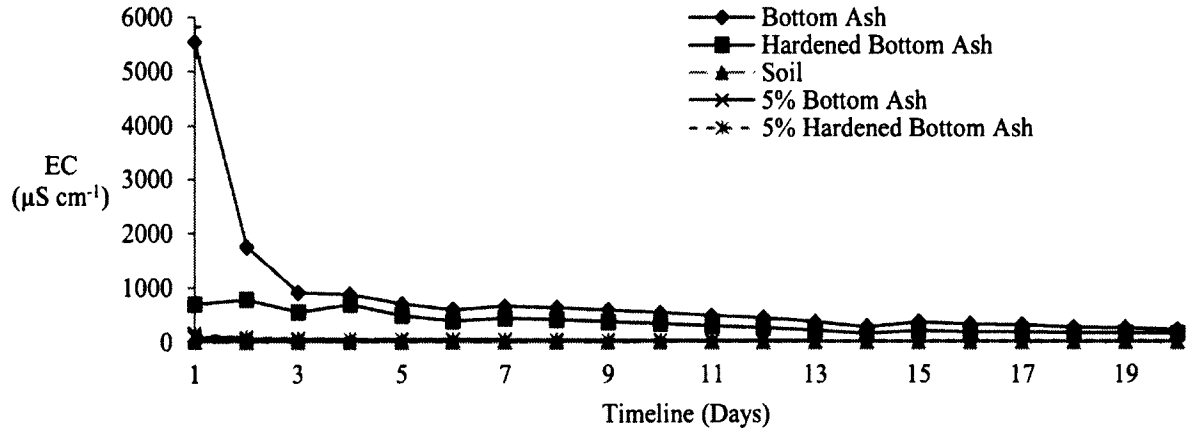

Figure 2.1 - Serial batch extraction of bottom ash, hardened bottom ash, soil, and 5% bottom and hardened bottom ash mixed with soil depicting electrical conductivity (EC) values over the twenty day timeline, n=4.

The aqueous concentrations for each element throughout the 20-cycle serial batch extraction are presented within Appendix A2 and only key trends are presented here. The following elemental concentrations for hardened bottom ash are presented relative to bottom ash. Values <1 (Table 2.5) indicate reduced leachability of an element in the hardened bottom ash treatment relative to bottom ash. Hardening reduced the leachability of Ba, Ca, Cd, Cu, Fe, Hg, Li, Mg, Mn, Ni, Pb, Sn, Sr, W, and Zn during the first day (Table 2.5). On day 10, hardening exhibited reduced leachability of Ag, As, B, Ca, Cd, Cu, Ni, P, Pb, Se, Si, Sr, V, and Zn relative to bottom ash. On day 20, hardened bottom ash reduced the leachability of Al, As, B, Ca, Cu, Fe, Hg, Mn, Na, P, Si, Sr, V, and W (Table 2.5). A few elements (B, Cr, Na, K, P, Se, and Si) also showed enhanced leaching due to hardening of bottom ash, but only during the initial few days (Table 2.5).

Table 2.5 – Ratio of HBA to BA for elemental concentrations in aqueous extracts during days 1, 2, 3, 4, 10, and 20 in the serial batch extraction study; lower values (e.g. < 1) indicate reduced elemental leaching due to HBA treatment.

Parameter	**Day 1**	**Day 2**	**Day 3**	**Day 4**	**Day 10**	**Day 20**
	HBA/BA	*HBA/BA*	*HBA/BA*	*HBA/BA*	*HBA/BA*	*HBA/BA*
Ag	2.75	n/d	n/d	n/d	0.115	3.51
Al	27.1	0.381	0.128	0.196	1.22	0.446
As	n/d	3.62	3.41	1.98	0.831	0.648
B	107	4.32	0.773	0.496	0.879	0.359
Ba	0.018	0.241	0.583	2.12	1.53	1.02
Ca	0.032	0.361	0.619	0.754	0.759	0.686
Cd	0.851	0.281	0.808	0.794	0.212	8.52
Cr	5.14	0.386	0.187	0.284	1.30	0.982
Cu	0.004	0.170	3.07	0.532	0.548	0.689
Fe	0.205	0.198	0.193	0.235	1.30	0.495
Hg	0.654	0.120	0.159	0.307	1.88	0.835
K	1.21	1.23	1.13	1.02	0.960	1.13
Li	0.62	0.99	1.84	1.34	2.22	1.71
Mg	0.499	1.49	2.10	1.64	1.48	1.73
Mn	0.453	0.632	0.592	0.462	1.50	0.472
Mo	1.14	0.243	0.331	0.658	1.41	1.52
Na	1.55	1.07	1.06	0.787	0.973	0.952
Ni	0.226	n/d	1.20	1.29	0.401	n/d
P	20.6	4.35	4.18	2.75	0.594	0.907
Pb	0.024	n/d	n/d	0.836	0.417	7.90
Sb	8.93	1.21	0.785	0.736	1.25	1.21
Se	2.33	0.243	0.777	n/d	0.777	n/d
Si	41.0	5.29	6.00	3.24	0.646	0.850
Sn	0.863	n/d	0.485	0.299	n/d	n/d
Sr	0.082	0.705	1.21	1.22	0.778	0.839
Ti	1.77	1.69	1.90	1.34	1.07	1.26
V	n/d	8.44	3.39	1.54	0.673	0.641
W	0.766	0.153	0.214	0.361	1.71	0.852
Zn	0.054	0.315	0.805	0.715	0.858	1.09

**Be, Bi, Co, Te, Th, Tl, U, Y, and Zr were undetected in the leachate by ICP-MS*

***n/d (not detected)*

Anions measured in extracted leachates (days one, ten and twenty) were Br^{-1}, Cl^{-1}, F^{-1}, NO_2^{-1}, NO_3^{-1}, PO_4^{-2}, and SO_4^{-2} (Figures 2.2 and 2.3). Alkalinity (reported as calcium carbonate equivalent; this was different from the measured CCE that was measured for the solid materials) of extracted leachates was also measured (Figure 2.4). Raw data of the anion analysis can be found in Appendix A1 (Tables A1.6 to A1.10).

Anion analysis of bottom ash and hardened bottom ash extracts showed that aqueous concentrations of bromine and phosphate were below detection limits of <0.01 ppm (Figure 2.2). Aqueous chlorine concentrations declined from 7.04 ppm to 0.45 ppm in bottom ash and from 5.30 ppm to 0.03 ppm for hardened bottom ash (Figure 2.3). Aqueous fluorine was only detected for day one and ten for both bottom and hardened bottom ash treatments (Figure 2.2). Aqueous nitrites were only detected for day one for both bottom and hardened bottom ash treatments (Figure 2.2). Aqueous sulphate concentrations and measured alkalinity of bottom ash and hardened bottom ash extracts decreased during the twenty days for bottom ash (sulphates from 5.26 ppm to 2.41 ppm, and alkalinity from 1617mg L^{-1} to 67.16mg L^{-1}) and hardened bottom ash (sulphates from 47.47 ppm to 0.74 ppm, and alkalinity from 187.0mg L^{-1} to 48.34mg L^{-1}). Bottom ash leachates had the highest measured alkalinity of all treatments (Figure 2.4).

Aqueous bromine concentration was below detection limit (<0.01 ppm) in the soil and ash-soil mix extracts (Figure 2.2). An increase over time of aqueous chlorine concentration was measured from the ash-soil extracts. Measured aqueous chlorine concentration declined over time in soil control extracts (Figure 2.3). Aqueous fluorine was detected for days one and ten for soil extracts (0.32 ppm and 0.01 ppm respectively, Figure 2.2), but was only detected for day one in both ash-soil extracts (Figure 2.2). Measured values for aqueous nitrite, nitrate, phosphate, sulphate, and alkalinity were found to be declining, as time progressed, in soil and ash-soil mixed treatments (Figures 2.2 to 2.4).

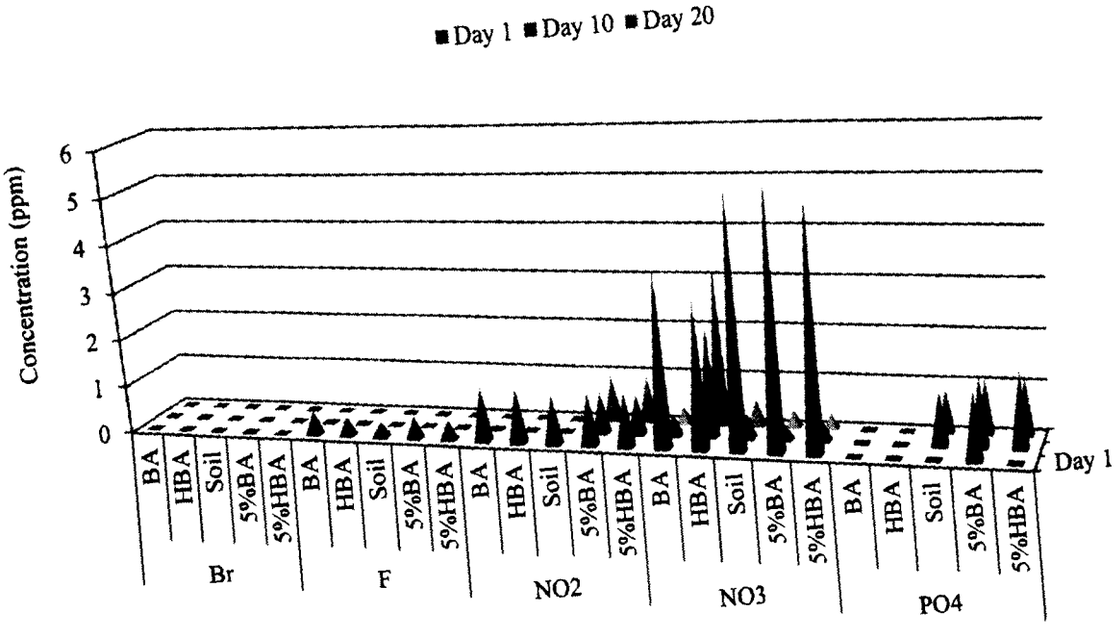

Figure 2.2 - Leachates from serial batch extraction showing bromine, fluorine, nitrite, nitrate and phosphate concentrations (ppm) contained within the extracts from days 1, 10 and 20 of the five treatments (BA, HBA, Soil, 5%BA and 5%HBA).

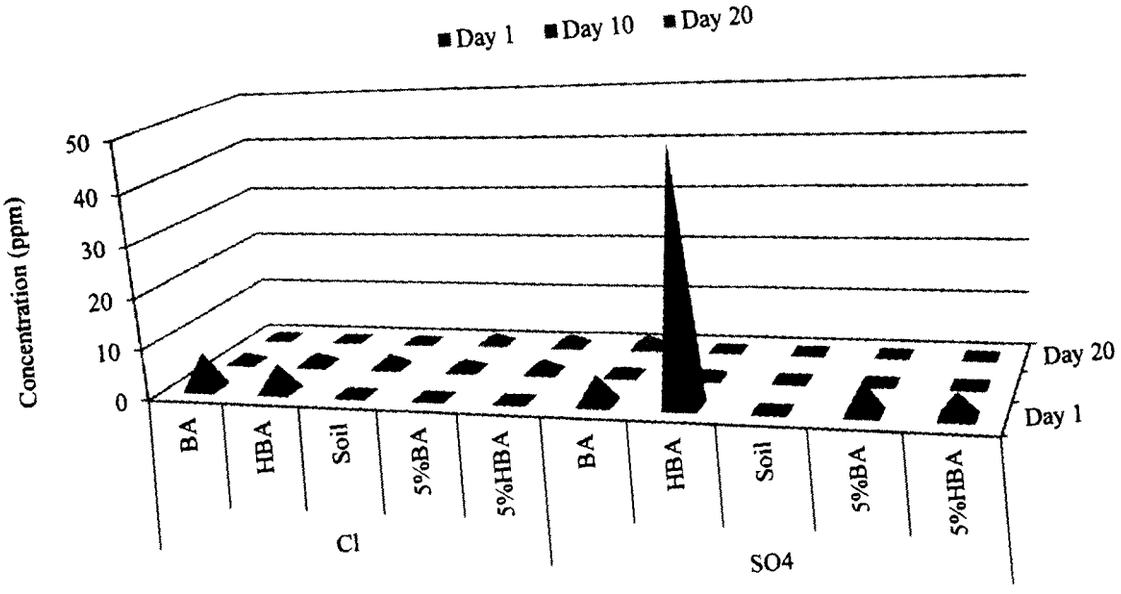

Figure 2.3 -Leachates from serial batch extraction showing chlorine and sulphate concentrations (ppm) contained within the extracts from days 1, 10 and 20 of the five treatments (BA, HBA, Soil, 5%BA and 5%HBA).

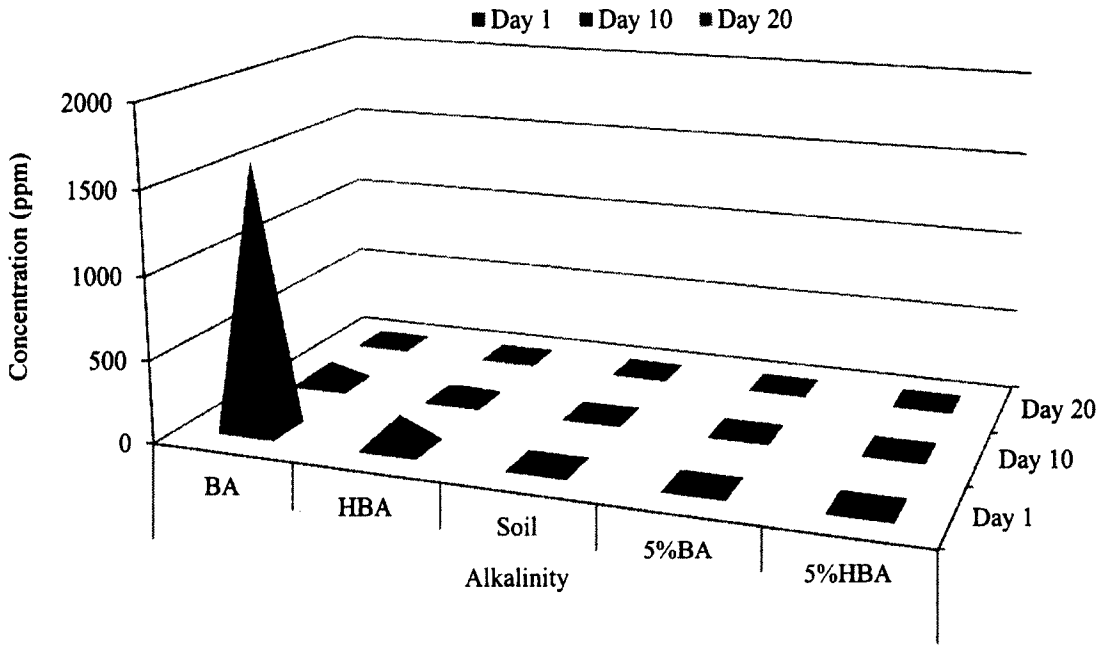

Figure 2.4 - Leachates from serial batch extraction showing alkalinity as $CaCO_3$ (ppm) contained within the extracts from days 1, 10 and 20 of the five treatments (BA, HBA, Soil, 5%BA and 5%HBA).

2.3.3 Geochemical Modelling of Serial Batch Extraction

Data obtained from the serial batch extraction analyses were entered into MINTEQ modelling to produce a saturation index for minerals (Tables 2.6 to 2.10). Analysis of the serial batch extraction data by MINTEQ predicted the presence of secondary minerals due to the oversaturation of major and minor elements contained within the extracts of the treatments. Some predicted minerals within the bottom ash and hardened bottom ash treatments were not predicted for the soil control treatment (Tables 2.6 to 2.10). These minerals were primarily calcium carbonate secondary minerals (aragonite, calcite, dolomite, and hydroxyapatite). Hydroxyapatite was also predicted to be present in the aqueous phase of ash-soil mixes, but not soil (Tables 2.9 and 2.10).

MINTEQ predicted that bottom ash and hardened bottom ash treatments contained many of the same secondary minerals; these minerals were primarily carbonate based (Table 2.6 and 2.7). Gibbsite was predicted to precipitate throughout in the HBA treatment, whereas gibbsite was only predicted to precipitate during the last day in the BA treatment. Hausmannite was only predicted during day ten for the HBA treatment but was prevalent throughout the BA treatment. Kaolinite was only predicted during day twenty, BA treatment, and predicted to precipitate on days ten and twenty for the HBA treatment. The formation of manganite, strontianite, tenorite, and witherite were predicted in the BA treatment and not the HBA treatment (Table 2.6 and 2.7).

Table 2.6 – Predicted mineral formation based on saturation index for bottom ash leachates during days 1, 10 and 20.

Day One		Day Ten		Day Twenty	
Mineral	**Sat. index**	**Mineral**	**Sat. index**	**Mineral**	**Sat. index**
Aragonite	2.91	Aragonite	1.47	Aragonite	1.15
Barite	0.348	Barite	-0.877	Barite	-0.381
Brucite	0.312	Brucite	-0.903	Brucite	-1.21
Ca3(PO4)2 (beta)	-1.13	Ca3(PO4)2 (beta)	0.121	Ca3(PO4)2 (beta)	-2.08
CaCO3xH2O(s)	1.72	CaCO3xH2O(s)	0.271	CaCO3xH2O(s)	-0.042
Calcite	3.06	Calcite	1.61	Calcite	1.30
Chrysotile	5.42	Chrysotile	7.86	Chrysotile	6.77
CoFe2O4(s)	20.1	CoFe2O4(s)	21.4	CoFe2O4(s)	22.9
Cupric Ferrite	9.35	Cupric Ferrite	9.50	Cupric Ferrite	11.0
Diaspore	-1.17	Diaspore	0.841	Diaspore	1.41
Dolomite (disordered)	1.43	Dolomite (disordered)	0.577	Dolomite (disordered)	0.579
Dolomite (ordered)	1.99	Dolomite (ordered)	1.14	Dolomite (ordered)	1.13
Ettringite	-1.87	Ettringite	-11.0	Ettringite	-12.3
Fluoroapatite	19.7	Fluoroapatite	16.8	Fluoroapatite	9.52
Akaganéite	1.82	Akaganéite	2.64	Akaganéite	3.29
Ferrihydrite	0.243	Ferrihydrite	0.858	Ferrihydrite	1.61
Ferrihydrite (aged)	0.753	Ferrihydrite (aged)	1.37	Ferrihydrite (aged)	2.12
Gibbsite (C)	-2.04	Gibbsite (C)	-0.028	Gibbsite (C)	0.544
Goethite	3.00	Goethite	3.61	Goethite	4.34
Gypsum	-2.57	Gypsum	-3.70	Gypsum	-3.54
Hausmannite	4.74	Hausmannite	1.83	Hausmannite	2.25
Hematite	8.39	Hematite	9.62	Hematite	11.1
Hydroxyapatite	10.1	Hydroxyapatite	10.3	Hydroxyapatite	6.55
Kaolinite	-10.7	Kaolinite	-0.646	Kaolinite	0.407
Lepidocrocite	2.19	Lepidocrocite	2.81	Lepidocrocite	3.50
Lime	-11.1	Lime	-14.4	Lime	-15.3
Maghemite	0.725	Maghemite	1.97	Maghemite	3.35
Magnesioferrite	7.48	Magnesioferrite	7.50	Magnesioferrite	8.67
Manganite	0.973	Manganite	0.183	Manganite	0.346
Portlandite	-1.08	Portlandite	-4.33	Portlandite	-5.25
Sepiolite	-2.97	Sepiolite	3.71	Sepiolite	2.93
Sepiolite (A)	-5.87	Sepiolite (A)	0.823	Sepiolite (A)	-0.026
SnSO4(s)	16.1	SnSO4(s)	19.3	SnSO4(s)	20.9
Strontianite	1.20	Strontianite	-0.105	Strontianite	-0.564
Tenorite(c)	0.754	Tenorite(c)	-0.334	Tenorite(c)	-0.284
Vaterite	2.48	Vaterite	1.04	Vaterite	0.726
Witherite	0.682	Witherite	-0.858	Witherite	-0.831

Table 2.7 – Predicted mineral formation based on saturation index for hardened bottom ash leachates during days 1, 10 and 20.

Day One		Day Ten		Day Twenty	
Mineral	**Sat. index**	**Mineral**	**Sat. index**	**Mineral**	**Sat. index**
Aragonite	1.31	Aragonite	1.20	Aragonite	0.898
CaCO3xH2O(s)	0.113	CaCO3xH2O(s)	0.007	CaCO3xH2O(s)	-0.294
Calcite	1.45	Calcite	1.35	Calcite	1.04
Chrysotile	5.02	Chrysotile	6.87	Chrysotile	6.16
CoFe2O4(s)	21.1	CoFe2O4(s)	22.3	CoFe2O4(s)	22.8
Cupric Ferrite	9.04	Cupric Ferrite	10.3	Cupric Ferrite	11.0
Diaspore	1.42	Diaspore	1.25	Diaspore	1.35
Dolomite (disordered)	-0.276	Dolomite (disordered)	0.353	Dolomite (disordered)	0.482
Dolomite (ordered)	0.282	Dolomite (ordered)	0.911	Dolomite (ordered)	1.04
Ettringite	-7.37	Ettringite	-12.3	Ettringite	-16.4
Fluoroapatite	13.6	Fluoroapatite	10.7	Fluoroapatite	8.55
Akaganéite	2.59	Akaganéite	3.21	Akaganéite	3.01
Ferrihydrite	0.703	Ferrihydrite	1.30	Ferrihydrite	1.60
Ferrihydrite (aged)	1.21	Ferrihydrite (aged)	1.81	Ferrihydrite (aged)	2.11
Gibbsite (C)	0.549	Gibbsite (C)	0.383	Gibbsite (C)	0.486
Goethite	3.46	Goethite	4.05	Goethite	4.33
Gypsum	-2.64	Gypsum	-3.71	Gypsum	-4.17
Hausmannite	-0.014	Hausmannite	0.278	Hausmannite	-2.0
Hematite	9.30	Hematite	10.5	Hematite	11.1
Hydroxyapatite	6.43	Hydroxyapatite	6.82	Hydroxyapatite	5.83
Kaolinite	-0.002	Kaolinite	0.374	Kaolinite	0.593
Lepidocrocite	2.65	Lepidocrocite	3.24	Lepidocrocite	3.48
Lime	-14.6	Lime	-15.1	Lime	-16.0
Maghemite	1.65	Maghemite	2.84	Maghemite	3.32
Magnesioferrite	6.41	Magnesioferrite	7.98	Magnesioferrite	8.33
MgCr2O4(s)	0.086	MgCr2O4(s)	-2.03	MgCr2O4(s)	-2.22
Portlandite	-4.57	Portlandite	-5.03	Portlandite	-5.96
Sepiolite	1.39	Sepiolite	3.22	Sepiolite	2.78
Sepiolite (A)	-1.5	Sepiolite (A)	0.330	Sepiolite (A)	-0.185
SnSO4(s)	20.6	SnSO4(s)	20.3	SnSO4(s)	21.2
Vaterite	0.881	Vaterite	0.774	Vaterite	0.474
Witherite	-1.26	Witherite	-0.848	Witherite	-0.924

The data from the addition of ash to soil (5%BA and 5%HBA treatments), as analyzed by MINTEQ, predicted new secondary minerals to form in the aqueous phase, as compared to secondary mineral predictions of the soil control (Tables 2.8 to 2.10). Chloropyromorphite and hydroxyapatite were predicted to precipitate in the ash-soil mixes but not in the soil control

(Tables 2.9 and 2.10).

Table 2.8 – Predicted mineral formation based on saturation index for soil leachates during days 1, 10 and 20.

Day One		Day Ten		Day Twenty	
Mineral	**Sat. index**	**Mineral**	**Sat. index**	**Mineral**	**Sat. index**
Akaganéite	7.02	Akaganéite	6.72	Akaganéite	6.14
Al(OH)3 (am)	0.326	Al(OH)3 (am)	-0.118	Al(OH)3 (am)	-0.645
Al(OH)3 (Soil)	2.84	Al(OH)3 (Soil)	2.40	Al(OH)3 (Soil)	1.87
Al2O3(s)	2.56	Al2O3(s)	1.67	Al2O3(s)	0.638
Al4(OH)10SO4(s)	3.46	Al4(OH)10SO4(s)	2.29	Al4(OH)10SO4(s)	-0.387
Boehmite	2.54	Boehmite	2.10	Boehmite	1.57
CoFe2O4(s)	23.0	CoFe2O4(s)	20.5	CoFe2O4(s)	18.9
Cupric Ferrite	13.8	Cupric Ferrite	10.8	Cupric Ferrite	9.16
Diaspore	4.26	Diaspore	3.82	Diaspore	3.29
Ettringite	-39.5	Ettringite	-51.2	Ettringite	-57.2
Ferrihydrite	3.99	Ferrihydrite	3.38	Ferrihydrite	2.97
Ferrihydrite (aged)	4.50	Ferrihydrite (aged)	3.89	Ferrihydrite (aged)	3.48
Gibbsite (C)	3.39	Gibbsite (C)	2.95	Gibbsite (C)	2.42
Goethite	6.75	Goethite	6.14	Goethite	5.70
Gypsum	-5.59	Gypsum	-7.11	Gypsum	-8.08
Halloysite	3.91	Halloysite	1.97	Halloysite	0.586
Hematite	15.9	Hematite	14.7	Hematite	13.8
Imogolite	4.88	Imogolite	3.47	Imogolite	2.24
Kaolinite	6.09	Kaolinite	4.15	Kaolinite	2.74
Lepidocrocite	5.93	Lepidocrocite	5.33	Lepidocrocite	4.86
Lime	-24.3	Lime	-26.4	Lime	-27.0
Maghemite	8.2	Maghemite	7.01	Maghemite	6.07
Magnesioferrite	6.09	Magnesioferrite	2.72	Magnesioferrite	1.38
MnHPO4(s)	-1.19	MnHPO4(s)	0.633	MnHPO4(s)	0.087
Plumbgummite	3.58	Plumbgummite	7.07	Plumbgummite	5.14
Portlandite	-14.2	Portlandite	-16.3	Portlandite	-16.9
Rutile	0.784	Rutile	0.919	Rutile	0.743
SnSO4(s)	28.8	SnSO4(s)	29.3	SnSO4(s)	29.1
Strengite	0.098	Strengite	2.53	Strengite	2.28

Table 2.9 – Predicted mineral formation based on saturation index for 5% bottom ash leachates during days 1, 10 and 20.

Day One		Day Ten		Day Twenty	
Mineral	**Sat. index**	**Mineral**	**Sat. index**	**Mineral**	**Sat. index**
Akaganéite	7.78	Akaganéite	7.96	Akaganéite	7.39
Al(OH)3 (am)	-0.168	Al(OH)3 (am)	-0.435	Al(OH)3 (am)	0.006
Al(OH)3 (Soil)	2.35	Al(OH)3 (Soil)	2.08	Al(OH)3 (Soil)	2.52
Al2O3(s)	1.57	Al2O3(s)	1.03	Al2O3(s)	1.94
Al4(OH)10SO4(s)	0.206	Al4(OH)10SO4(s)	-3.05	Al4(OH)10SO4(s)	-1.14
Boehmite	2.05	Boehmite	1.78	Boehmite	2.23
Calcite	-0.973	Calcite	-1.46	Calcite	-2.97
Chloropyromorphite(c)	0.835	Chloropyromorphite(c)	2.93	Chloropyromorphite(c)	3.44
CoFe2O4(s)	28.2	CoFe2O4(s)	28.5	CoFe2O4(s)	25.3
Cupric Ferrite	18.3	Cupric Ferrite	18.3	Cupric Ferrite	15.7
Diaspore	3.77	Diaspore	3.50	Diaspore	3.94
Ettringite	-23.7	Ettringite	-30.3	Ettringite	-39.6
Fluoroapatite	13.4	Fluoroapatite	6.97	Fluoroapatite	-2.96
Ferrihydrite	5.30	Ferrihydrite	5.31	Ferrihydrite	4.56
Ferrihydrite (aged)	5.81	Ferrihydrite (aged)	5.82	Ferrihydrite (aged)	5.07
Gibbsite (C)	2.90	Gibbsite (C)	2.63	Gibbsite (C)	3.07
Goethite	8.06	Goethite	8.07	Goethite	7.29
Gypsum	-3.44	Gypsum	-5.54	Gypsum	-7.05
Halloysite	3.48	Halloysite	2.26	Halloysite	3.03
Hematite	18.5	Hematite	18.5	Hematite	17.0
Hydroxyapatite	5.02	Hydroxyapatite	4.74	Hydroxyapatite	-0.997
Imogolite	4.17	Imogolite	3.29	Imogolite	4.11
Kaolinite	5.65	Kaolinite	4.44	Kaolinite	5.19
K-Jarosite	0.142	K-Jarosite	-4.75	K-Jarosite	-7.24
Lepidocrocite	7.25	Lepidocrocite	7.26	Lepidocrocite	6.44
Lime	-20.8	Lime	-20.8	Lime	-22.6
Maghemite	10.8	Maghemite	10.9	Maghemite	9.24
Magnesioferrite	11.6	Magnesioferrite	11.4	Magnesioferrite	8.15
MnHPO4(s)	1.83	MnHPO4(s)	2.00	MnHPO4(s)	1.66
Plumbgummite	4.41	Plumbgummite	3.56	Plumbgummite	6.45
Portlandite	-10.8	Portlandite	-10.7	Portlandite	-12.5
Rutile	0.997	Rutile	0.819	Rutile	0.743
SnSO4(s)	27.5	SnSO4(s)	25.3	SnSO4(s)	25.7
Strengite	1.78	Strengite	1.53	Strengite	2.03

Table 2.10 – Predicted mineral formation based on saturation index for 5% hardened bottom ash leachates during days 1, 10 and 20.

Day One		Day Ten		Day Twenty	
Mineral	**Sat. index**	**Mineral**	**Sat. index**	**Mineral**	**Sat. index**
Akaganéite	7.28	Akaganéite	7.86	Akaganéite	7.45
Al(OH)3 (Soil)	1.90	Al(OH)3 (Soil)	2.32	Al(OH)3 (Soil)	2.50
Al2O3(s)	0.668	Al2O3(s)	1.50	Al2O3(s)	1.91
Boehmite	1.60	Boehmite	2.01	Boehmite	2.21
Calcite	-0.413	Calcite	-2.21	Calcite	-3.19
Chloropyromorphite(c)	-8.87	Chloropyromorphite(c)	3.88	Chloropyromorphite(c)	3.48
CoFe2O4(s)	26.4	CoFe2O4(s)	27.4	CoFe2O4(s)	25.4
Cupric Ferrite	16.6	Cupric Ferrite	17.5	Cupric Ferrite	15.7
Diaspore	3.32	Diaspore	3.74	Diaspore	3.92
Ettringite	-24.0	Ettringite	-33.5	Ettringite	-38.6
Fluoroapatite	4.12	Fluoroapatite	2.82	Fluoroapatite	-4.07
Ferrihydrite	4.71	Ferrihydrite	5.07	Ferrihydrite	4.60
Ferrihydrite (aged)	5.22	Ferrihydrite (aged)	5.58	Ferrihydrite (aged)	5.11
Gibbsite (C)	2.45	Gibbsite (C)	2.87	Gibbsite (C)	3.05
Goethite	7.46	Goethite	7.83	Goethite	7.33
Gypsum	-3.27	Gypsum	-5.89	Gypsum	-6.52
Halloysite	2.93	Halloysite	2.94	Halloysite	3.12
Hematite	17.3	Hematite	18.0	Hematite	17.1
Hydroxyapatite	-1.47	Hydroxyapatite	2.38	Hydroxyapatite	-1.57
Imogolite	3.44	Imogolite	3.87	Imogolite	4.14
Kaolinite	5.11	Kaolinite	5.12	Kaolinite	5.28
Lepidocrocite	6.65	Lepidocrocite	7.02	Lepidocrocite	6.48
Lime	-20.8	Lime	-21.6	Lime	-22.7
Maghemite	9.65	Maghemite	10.4	Maghemite	9.32
Magnesioferrite	10.7	Magnesioferrite	10.2	Magnesioferrite	8.15
MnHPO4(s)	-1.07	MnHPO4(s)	2.04	MnHPO4(s)	1.71
Quartz	0.074	Quartz	-0.337	Quartz	-0.439
Plumbgummite	-2.08	Plumbgummite	5.31	Plumbgummite	6.53
Portlandite	-10.7	Portlandite	-11.6	Portlandite	-12.7
Rutile	0.581	Rutile	0.858	Rutile	0.786
SnSO4(s)	27.6	SnSO4(s)	25.8	SnSO4(s)	26.4
Strengite	-1.05	Strengite	1.96	Strengite	2.17

2.4 DISCUSSION

Hardening of bottom ash was shown to be a means of improving physical properties and reducing the reactivity of components contained within gasifier bottom ash. This hardening process altered the mineralogy of the ash and this study hypothesized that the leachability of several elements would be altered relative to that of the loose, untreated, bottom ash. Few studies have examined the long-term weathering of ashes in the environment; the serial batch extraction was conducted to predict elemental loss from ash materials over the long-term (e.g. if landfilled or stockpiled). These ash materials were also mixed with fine-textured soil, as ash may be used as an amendment to improve soil conditions in agricultural or forest applications and relevant studies in the literature have usually focused on ash addition to coarse-textured soils (Fransman and Nihlgard, 1995; Kahl et al., 1996; Piirainen, 2001; Saarsalmi et al., 2005). It was expected that fine-textured soil would alter the mobility of elements originating from these ash materials. The geochemical model MINTEQ was used to predict the mineralogy of the ashes, and how mineralogy of the receiving soil would be influenced by ash additions. However, MINTEQ assumes equilibrium and does not take kinetics into consideration during its calculations. Therefore, a mineral may be predicted to dissolve or precipitate out of solution, but the time for that to occur is not known. This may take hours or months for the predicted reactions to occur.

2.4.1 Initial Characterization and Composition of Ashes

The elemental composition of the bottom ash used in this study was typical of other wood-biomass ashes reported in literature (Steenari and Lindqvist, 1997; Steenari et al., 1999; Liao et al., 2007). Bottom ash and hardened bottom ash were found to be primarily composed of the elements Ca, Fe, K, Al, Mg, Mn, P, Na, Ba, and S (major inorganic elements defined here as being greater than 1000 mg kg^{-1} in the solid phase). The remainder was a composition of As, B, Co, Cr, Cu, Mo, Ni, Sr, and Zn (Table 2.0). According to the Soil Amendment Code of Practice

(SACoP) there are 11 metals of concern (Environmental Management Act, 2007), of which the elements As, Co, Cr, Cu, Mo, Ni, and Zn were found to be contained in ash. The other 4 metals, Cd, Pb, Hg, and Se were below ICP detection limits (Table 2.0). The hardening process did not alter the non-organic elemental composition (Table 2.0), but it was expected that the mineralogical composition changed. In non-hardened bottom ash, the minerals expected to dominate were the oxides of the major inorganic elements; this is a result of the burning process (Steenari and Lindqvist, 1997). Calcium makes up a large portion of these mineralogical components as calcium oxide (CaO) and calcite ($CaCO_3$) (Steenari and Lindqvist, 1997). In hardened ash the formation of cement-type minerals gypsum, calcite, ettringite, portlandite, and other sulphate bearing minerals was expected to occur (Steenari and Lindqvist, 1997; Demeyer et al., 2001).

2.4.2 Simulated Long-Term Weathering of Ash – Hardened versus Non-Hardened

The batch extraction experiment simulated the long-term weathering of ash if it were to come into contact with water. In non-hardened ash, the initial leachate composition was dominated by Ca, K, Si, Al, Ba, Na, and SO_4^{-2} (Appendix A2). These high concentrations were accompanied by an elevated electrical conductivity, which is an index of total dissolved solids (Figure 2.1). The initial elevated concentration of Ca, K, Al, Ba, Na, and SO_4^{-2} rapidly declined over time as highly soluble components were leached from bottom ash (Appendix A2). This rapid decline in concentration was consistent with other leachate studies (Dudas, 1981; Steenari and Karlsson, 1999; Talbot, Anderson and Andren, 1978; Zevenbergen et al., 1998). In comparison, elements and anions leached from other ashes (municipal solid waste incinerator (MSWI) bottom ashes, grate fired boiler ashes, and coal fly ashes) were Ca, K, Si, Al, Na, and SO_4^{-2}, with some also reporting Fe, Mg, and Cl^{-1} to have leached preferentially (Dudas, 1981; Steenari and Karlsson, 1999; Talbot, Anderson and Andren, 1978; Zevenbergen et al., 1998). With the

exception of large amounts of Fe, Mg, and Cl^{-1} leached from several ashes, as reported by other studies, many of the constituents leached from bottom ash in this study were similar to other studies (Dudas, 1981; Steenari and Karlsson, 1999; Talbot, Anderson and Andren, 1978; Zevenbergen et al., 1998).

The hardening process influenced the leachate chemistry during the long-term weathering study, especially during the initial stages of the experiment. For example, compared to non-hardened ash, the electrical conductivity (Figure 2.1), and aqueous concentrations of Al, Ba, Ca, Cu, Hg, Sr, and Zn were much lower from hardened bottom ash extracts (Table 2.5). However, some elements exhibited a higher initial aqueous concentration in the hardened ash treatment. These elements were B, Cr, K, Mo, Na, P, Sb, Se, Si, and SO_4^{-2} (Table 2.5, Figure 2.3). As the weathering progressed, the aqueous concentrations of many elements were similar in the hardened and non-hardened bottom ash treatments (Table 2.5).

Observations made from the serial batch extraction were used to explain some of the leaching characteristics for elements of agronomic value (Ca, Na, K, and S). The amount of calcium leached from bottom ash was extensive (Table 2.2 and Figure A2.7). However, hardening reduced the amount of Ca leached from ash by a significant amount, especially during the initial serial batch extracts (Figure A2.7). Throughout the entire weathering process, the amount of Ca lost was calculated to be 27% for bottom ash and 17% for hardened bottom ash; these values were similar to the 2% to 19% Ca leached as seen by Steenari et al. (1999) (grate-fired boiler bottom ashes). The insoluble nature of cement based minerals (primarily Ca based) that may have formed during hardening likely contributed to lower Ca dissolution from hardened bottom ash. These formed minerals were likely to be gypsum, portlandite, calcite, calcium silicate, and possibly ettringite (Steenari and Lindqvist, 1997; Demeyer et al., 2001).

Sodium and potassium comprised 2% of the bottom ash solid phase (Table 2.0). The percentage of Na (13% BA and 15% HBA) and K (19% BA and 23% HBA) leached from the ashes were found to be similar to Steenari et al. (1999) and a little higher than weathered fly ashes found by Neupane et al. (2012). Following hardening, the amount of Na and K initially leached from bottom ash increased compared to non-hardened ash (Figures A2.14 and A2.19). Higher aqueous concentrations of Na and K may have been due to the soluble hydroxides and sulphate salts of Na and K that were not as prevalent in non-hardened bottom ash. Sodium and K are in their oxide form, K_2O and Na_2O, within bottom ash, and form their hydroxides when exposed to water when ash is hardened (Gori et al., 2011). Due to a high pH environment and the presence of sulphates within ash (as measured in the aqueous phase; Figure 2.3), hardening may have also resulted in the formation of Na and K sulphates (Na_2SO_4 and K_2SO_4) (Gori et al., 2011; Ring et al., 2006). The greater amount of soluble sodium and potassium hydroxides and sulphates likely present in hardened bottom ash would have resulted in a spike in the initial aqueous concentrations of Na and K compared to bottom ash extracts, as was found in the serial batch extraction analysis (Figures A2.14 and A2.19).

Aqueous sulphur was not able to be determined by ICP, but sulphate ions were determined by ion chromatography during days one, ten and twenty of the serial batch extracts (Figure 2.3). Total sulphur content in bottom ash and hardened bottom ash solid phase was also measured by ICP-OES (Table 2.0). Using the measured sulphur contained in bottom ash and hardened bottom ash, an estimation of total sulphur loss was determined to be 27% for bottom ash and 30% for hardened bottom ash treatments (Table 2.2). Aqueous extracts from hardened bottom ash were found to contain higher aqueous sulphate concentrations than bottom ash extracts (Figure 2.3). Compared to bottom ash, the increased amount of sulphate leached from hardened bottom ash may have been due to the dissolution of gypsum and soluble salts of

Na_2SO_4 and K_2SO_4 that would have formed during hardening compared to non-hardened bottom ash. The formation of Na_2SO_4 and K_2SO_4 in hardened wood based ashes has also been reported by Ring et al., (2006), along with calcium sulphate (i.e. gypsum) by others (Steenari and Lindqvist, 1997).

Unlike the dominating ions of Ca, K, Si, Al, Na, and SO_4^{-2} in solution, the aqueous concentrations of environmentally sensitive trace elements and anions were generally low in the non-hardened and hardened bottom ashes. Of the trace elements, aqueous concentrations were greatest for Cr, Cu, Mo, and Hg. High pH of the aqueous environment (Figure 2.0), low solid phase concentration of trace elements (Table 2.0), and the adsorption of trace elements to formed secondary minerals likely attributed to low aqueous concentrations of the many measured trace elements (Chimenos et al., 2000; Warren and Dudas, 1985; Steenari and Karlsson, 1999; Talbot, Anderson and Andren, 1978; Neupane et al., 2012). As with the major inorganic elements, aqueous concentrations of trace elements were generally greatest during the initial serial batch extracts. Most trace elements had very low dissolution and likely persisted within the solid phase, or were adsorbed into the formation of secondary minerals, and continue to persist in the solid phase (McBride, 1994; Neupane et al., 2012). For example, low zinc leaching (Table 2.5) might be attributed to negatively charged particles present in the aqueous phase during weathering of bottom ash. Bottom ashes tend to contain Fe-, and Al-hydroxides, and in an alkaline ash-water system, these hydroxides can form soluble species that are negatively charged, which can be incorporated into neoformations (i.e. $Al(OH)_4^-$, and $Fe(OH)_4^-$) (McBride, 1994). Neoformations are the precipitation of new secondary minerals that form at low temperatures as a result of various ions weathered from primary minerals (McBride, 1994). These negatively charged species could attract dissolved zinc, as Zn^{2+}, to the surface of those particles, either through ion-exchange, or direct adsorption to the mineral. Other charged ions (i.e. dissolved trace elements in

solution) would also tend to co-precipitate in this manner as well. This is likely to have occurred with many of the trace metals found from weathering bottom and hardened bottom ash (Appendix A2).

Of the measured anions, SO_4^{-2}, Cl^{-1}, and NO_3^{-1} dominated, but decreased over time (Figures 2.2 and 2.3). The trace element and anion concentrations can be put into perspective by comparing them with maximum levels allowable for aquatic systems and drinking water standards. This type of comparison is also relevant for situations where large quantities of water in contact with ash may make its way into a surface water or ground water. The British Columbia Contaminated Sites Regulation, BCCSR, (Schedule 6) contains allowable limits for many of the trace elements and some major inorganic elements contained within an aqueous system (Chapter 3; Table 3.2).

This study was not focused on water quality and its respective limits, nor was there any field experiments performed, and a comparison to water standards is only to put perspective on elemental concentrations found in the extracts during the serial batch extractions. The allowable limits of Cr, Cu, and Hg for freshwater aquatic life were only exceeded briefly during the first day of the serial batch extraction for both ashes and fell below allowable limits thereafter. Only aqueous concentrations of Cl^{-1}, NO_3^{-1}, and NO_2^{-1} continually exceeded concentrations set out by BCCSR for aquatic life. Generally, the limits exceeded by ash treatments were short lived as sharp declines in concentration of the above mentioned (few) elements fell below allowable limits set by the British Columbia Contaminated Sites Regulation (Schedule 6).

Over the course of the weathering study, the overall loss of elements from the solid phase was generally similar in the two ash types (Table 2.2). The weathering experiment resulted in a large percent loss of some elements (Ca, B, Mo, S, Sr, Ba, K, and Na), while other elements (Fe, Mg, Mn, P, Al, and the rest of the trace elements) only exhibited slight losses (Table 2.2).

Interestingly, even though bottom ash and hardened bottom ash contained high concentrations of Fe, Mg, Mn, and P, very little loss was observed from these elements (Table 2.2). This observation was also reported in other studies (Steenari and Karlsson, 1999; Talbot, Anderson and Andren, 1978; Zevenbergen et al., 1998). Low leachability of Fe, Mg, Mn, and P may have been due to high pH conditions and the continual formation of secondary minerals decreasing solubility as revealed through MINTEQ analysis.

2.4.3 MINTEQ Analysis of Serial Batch Extraction - Hardened versus Non-Hardened

Saturation index (SI) is an index value that is used to determine whether a particular mineral is predicted to dissolve or precipitate in water. SI is calculated by comparing the chemical activities, ion activity product (IAP) and solubility product (K_s), of dissolved ions for a desired mineral; in MINTEQ the calculation for SI = log(IAP) – log(K_s). A saturation index <0 (logIAP < logKs) indicates undersaturation of a mineral, meaning that it may be dissolved in solution, whereas a value >0 (logIAP > logK_s) indicates oversaturation of a mineral, meaning that the mineral may have precipitated in solution. A saturation index of 0 indicates that the predicted mineral in solution is in equilibrium. SI values that are at or nearing equilibrium are said to be the main solubility-controlling minerals in an aqueous solution (Meima et al., 2002).

2.4.3.1 Changes in Secondary Mineral Formation Over Time

Analysis of the data from the serial batch extraction by MINTEQ revealed a few notable changes in the formation of secondary minerals between hardened and non-hardened bottom ash. In bottom ash, barite, brucite, calcite (hydrate), strontianite, tenorite, and witherite were predicted to be become thermodynamically unstable (i.e. SI < 0) as time progressed, indicating their potential dissolution. Disapore, gibbsite, and sepiolite were predicted minerals in a bottom ash/water mixture that started thermodynamically unstable (i.e. undersaturated) but were predicted to become stable (i.e. saturated over time). However, in hardened bottom ash calcite

(hydrate) was predicted to be thermodynamically unstable indicating dissolution. Dolomite (disordered) and kaolinite began thermodynamically unstable but were predicted to become stable.

Looking at the SI of several key elements (Ca, Fe, Mn, and P) that were prominent within the predicted secondary mineral formation of both bottom ash and hardened bottom ash we can obtain further insight into the leaching observations made from the serial batch extraction. Of the predicted mineral formations containing Ca (aragonite, calcium phosphate, calcite, dolomite, fluoroapatite, hydroxyapatite, and vaterite), their SI values were decreasing over time, which could potentially indicate dissolution of Ca for bottom ash and hardened bottom ash (Table 2.6 and 2.7). More specifically, possible solubility-controlling minerals for Ca dissolution from bottom ash may be from calcite-type minerals (aragonite, calcite-hydrate, and vaterite), apatite, and dolomite at high pH, as many of these predicted minerals were nearing equilibrium as time progressed (Table 2.6). Compared to non-hardened bottom ash, calcite is likely more dominant in the solid phase of hardened bottom ash, and was found to be the primary solubility-controlling mineral for Ca dissolution as calcite, calcite-hydrate, aragonite, and vaterite (all calcite-type minerals); these calcite minerals were much closer to equilibrium, over time, compared to that of non-hardened bottom ash (Table 2.7). Other possible solubility-controlling minerals in an ash-water system that have been reported in literature have been portlandite ($Ca(OH)_2$), lime (CaO), and possibly gypsum ($CaSO_4$) (Meima and Comans, 1997 and 1998). As with Ca, other solubility-controlling minerals for Mg (brucite), Fe (ferrihydrite), P ($Ca_3(PO_4)_2$), and potentially Mn (manganite) were determined by modelling for bottom ash (Table 2.6). Potential solubility controlling minerals predicted for hardened bottom ash for Fe and Mn were ferrihydrite and hausmannite (Table 2.7).

Of the predicted mineral formations containing Fe from both ash treatments (cobalt ferrite, cupric ferrite, akaganéite, ferrihydrite, goethite, hematite, lepidocrocite, and maghemite), their SI values were increasing over time, which could potentially indicate a greater likelihood of mineral formation that would keep Fe dissolution low (Table 2.6 and 2.7); as was observed for Fe leaching during the serial batch extraction. Of Mn and P, predicted minerals containing these elements showed slowly declining SI values over time, however these SI values were very high compared to other predicted minerals; this could potentially indicate very slow Mn and P dissolution. In addition, as P was leached from ash, secondary minerals of P can form as Al, Fe, and Ca phosphates when they react together with any of these major inorganic elements in solution and are sparingly soluble (namely apatite, fluoroapatite, and hydroxyapatite; Table 2.6 and 2.7) (McBride, 1994).

2.4.3.2 Changes in Secondary Minerals Between Hardened and Non-Hardened Ash

More secondary minerals were predicted to form in an aqueous environment containing bottom ash, which may be due to the greater influx of dissolved ions in solution from bottom ash compared to hardened bottom ash. The greater influx of ions in solution was observed from the measured electrical conductivity measurement taken from bottom ash extracts (Figure 2.1). More ions in solution would result in a greater amount of predicted secondary minerals to precipitate. Differences that were predicted were the formation of barite, brucite, calcium phosphate, manganite, strontianite, tenorite, and witherite in bottom ash compared to hardened bottom ash. These were Mg, Ba, Ca, Mn, Sr, and Cu based minerals, and their predicted mineralogy may be due to a higher aqueous concentration of these elements leached from bottom ash compared to hardened bottom ash.

2.4.4 Ash as a Soil Amendment

The high pH of bottom ash makes it ideal for use as a soil amendment to ameliorate acidic forest or agricultural soils. The calcium carbonate equivalency of bottom ash and hardened bottom ash were 30.5% and 29.2% respectively (Table 2.0). Bottom ash also has other properties beyond that of a simple liming agent such as an agricultural limestone, which is a liming agent that contains other added plant nutrients. In addition to a high concentration of calcium, bottom ash and hardened bottom ash are relatively high in other plant macro-nutrients such as Fe, K, Mg, Mn, P, Na, and S (Table 2.0). Only N is lacking in significant concentrations. Many of these major inorganic elements (primarily macro-nutrients, Ca, K, Na, and S) were readily leached from bottom ash (Table 2.2). This could be advantageous if the ash was intended for use as a soil amendment. In general, hardening produced a slower release of nutrients as compared to untreated ash (Figure 2.1 and Table 2.5); this may be desirable in some conditions where salinity of the receiving soil may be of concern. Some other concerns with bottom ash may be from elevated trace elements and the presence of products from incomplete combustion (e.g. PAHs). However, products of incomplete combustion were not studied in this experiment, but a sample collected at UNBC containing low carbon ash (collected July 13, 2012) contained negligible PAHs, dioxins, and furans (unpublished data). It is likely that the same inference could be made about the bottom ash used in this study.

Bottom ash intended for use as a soil amendment must meet certain compositional criteria as many jurisdictions have maximum allowable concentrations for environmentally sensitive elements. For example, within western Canada (British Columbia and Alberta) the BC Soil Amendment Code of Practice (SACoP), and Alberta Environment have maximum allowable elemental limits for chemical constituents (Table 2.0). Guidelines also exist in the European countries of Denmark, Finland, and Sweden (Table 2.0).

The BC SACoP requires a waste material be measured for its As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Se, and Zn content, while Alberta Environment (regarding ash as a liming agent) only requires a waste material's content of B, Cd, and Zn to be determined. Both bottom ash and hardened bottom ash used in this study did not exceed any trace element limits as set out by the SACoP. However, B concentrations in bottom ash (140 mg kg^{-1}) and hardened bottom ash (120 mg kg^{-1}) did not meet the Alberta Environment criteria of 43 mg kg^{-1} (dry weight). Furthermore, Ni (61ppm for BA, and 56ppm for HBA) exceeded the maximum allowable limit for Denmark (30ppm allowable), and Zn (148ppm for BA, and 94ppm for HBA) did not meet the minimum limit for Sweden (500ppm minimum) in forestry applications (Table 2.0). It is probable that bottom ash in its hardened state would make a good soil amendment or liming agent. Hardening of bottom ash was shown to significantly reduce the electrical conductivity of an aqueous solution in contact with ash (i.e. lower concentration of ions released into the aqueous phase), likely due to newly formed secondary minerals that slowly release their respective elements.

Another concern with use of biomass ashes as a soil amendment is its reactivity based on measured electrical conductivity of an aqueous solution in contact with ash, as defined by Haglund (2008). Haglund (2008) indicated that recycling ash to forest floors (not applicable to agricultural land) can be separated into three categories based on reactivity; A (<2800 mS m^{-1}), B (2800 – 3200 mS m^{-1}) and C (3200 – 3600 mS m^{-1}) (C being the most reactive). Their recommended rates for a, one-time, 10 year application include 2-3 ton ha^{-1} (A), 1-2 ton ha^{-1} (B), and <1 ton ha^{-1} (C). According to numbers given by Haglund (2008), BA (989 mS m^{-1}) and HBA (309 mS m^{-1}) fell within category A, and both ashes would be appropriate for recycling to forest floors, based on reactivity (Table 2.0).

2.4.5 Simulated Long-Term Weathering of Ash-Soil Mixtures

Ash components can undergo a number of reactions upon addition to soil. These include adsorption of leached ash constituents to the soil profile (Fransman and Nihlgard, 1995; Pitman, 2006; Ring, 2006), and the binding of leached elements, such as Ca, to organically bound P in soils (Jacobson et al., 2004). In general, these reactions are expected to reduce the solution concentrations of elements present compared to ash-only mixtures, but may not always be the case. The addition of ash to soil may also increase concentrations of aqueous species relative to the untreated soil such as Ca, Mg, P, and K (Fransman and Nihlgard, 1995; Jacobson et al., 2004). Few studies in literature report on the influence of ash addition to fine-textured soils, or changes which may occur over the long-term. The purpose of the long-term weathering experiment with ash and soil was designed to determine how major and minor elemental leaching may be altered when ash was mixed with soil. Hardened and non-hardened bottom ashes in this study were added to a fine-textured soil, typical of many soils found in north-central British Columbia.

It was expected that a fine-textured soil would behave similar to coarse-textured soils that have had ash applications (Fransman and Nihlgard, 1995; Kahl et al., 1996; Piirainen, 2001; Saarsalmi et al., 2005). That is, the fine-textured soil would reduce the concentration of elements released from ash into an aqueous system. In general, the leachability of ash was reduced when mixed with soil, after the initial dissolution of the more soluble constituents contained within ash. In addition to any possible dilution effects, the reduced leaching of many elements, both major and minor, may have been due to three mechanisms. First, secondary mineral formation (i.e. precipitation reactions) as a result of ions in solution likely reduced aqueous phase concentrations (MINTEQ predictions). Second, soil attenuated the ability for many elements to be leached likely through adsorption reactions, which was commonly reported in field studies looking at ash

application to coarse-textured soils (Fransman and Nihlgard, 1995; Kahl et al., 1996; Piirainen, 2001; Saarsalmi et al., 2005). Third, secondary minerals were likely causing absorption and adsorption of many minor elements.

Ash addition to soil resulted in a long-term elevation of pH relative to the non-treated soil (Figure 2.0). Both, bottom ash and hardened bottom ash were observed to have similar leaching characteristics when applied to soil. Electrical conductivity of solution extracts were initially high, but decreased as soluble constituents were leached from the ash, as was found in the ash-only treatment (Figure 2.1). Initially, some major inorganic elements (Al, Ca, K, Mg, Na, P, Si, Sr, and SO_4^{-2}) and environmentally sensitive elements (As, Cr, Hg, and Mo) were measured to have elevated aqueous concentrations compared to the soil control, but decreased after several leaching cycles. The ability for soil to reduce the aqueous concentration of elements, from the leached bottom ash, was observed by ICP analysis of the ash-soil extracts (Appendix A2) and overall lowering electrical conductivity measurements that converged with soil control measurements (Figure 2.1).

Some elements (As, Mg, and P) were found to have increased aqueous concentrations relative to both control soil and the ash-only treatments, even after several leaching cycles. This increased solubility of As, Mg, and P was likely due to the lower pH of the ash-soil mixtures, relative to ash-only (Figure 2.0). This is significant, especially for P, as it is often the most limiting nutrient in many ecosystems (McBride, 1994). The availability of ash-derived P increased as pH decreased to neutral values (Figure A2.21). It is likely that P is present as apatites in ash (Yusiharni and Gilkes, 2012), which have very low solubility at high pH, but increase in solubility as the environment becomes neutral to acidic (McBride, 1994). Although soluble As concentrations increased in ash treatments, the aqueous concentrations were still well below Canadian guidelines for aquatic systems and drinking water. The slight increase of arsenic

leached from ash-soil mixes was probably attributed to the lower pH environment and lack of iron dissolution (Figure 2.0 and Figure A2.2). Chapter 3 reveals how neutral pH can cause enhanced As solubility from pH 5 to 7.5 in bottom ash. Together, the lack of iron leaching and lower pH increased arsenic solubility in ash-soil mixes, as secondary minerals can form with arsenic and iron (Theis and Wirth, 1977). The formation of iron secondary minerals at very high pH would explain the low solubility of arsenic in ash-only treatments (Tables 2.6 to 2.10) (Chapter 3). In contrast, iron solubility was slightly hindered at pH 5 to 7 (Chapter 3). Incidentally, arsenic had highest solubility at this pH (approx. pH 6-8) during the serial batch extraction of soil-ash mixes (Figure A2.2).

Generally, soil reduced the ability for minor elements (Co, Cu, Pb, Zn, Cd, Ni, and Se), major inorganic elements (Al, K, Mg, Na, Si, and Sr), and the anion SO_4^{-2} in ash-soil treatments to be leached from ash after several leaching cycles, eventually showing that aqueous concentrations in ash-soil mixes were similar to soil control (Appendix A2). The formation of secondary minerals from ions in solution, and the sorption influence of soil and secondary minerals likely attributed to the low aqueous concentration of the many trace elements seen in the treatments containing ash and soil (Appendix A2). Neupane et al. (2012) also revealed that the slow but persistent dissolution of elements through weathering (even at low concentrations) may be due to the adsorption of these elements to formed secondary minerals. Therefore, the probable adsorption by soil particles and secondary mineral formation (from saturated major inorganic elements) was likely the reason for the low aqueous concentration of the trace elements.

2.4.6 Concluding Thoughts

Bottom ash and hardened bottom ash were primarily composed of Ca, Fe, K, Al, Mg, Mn, P, Na, Ba, and S, with the remainder being composed of B, Sr, As, Co, Cr, Cu, Mo, Ni, and Zn. Long-term weathering revealed that Ca, K, Si, Al, Ba, Na, and SO_4^{-2} dominated the bottom ash leachate, and was accompanied by a high electrical conductivity. Initial elevated aqueous concentrations rapidly declined as highly soluble components were leached from ash. Hardening influenced the initial stages of weathering by reducing electrical conductivity of the aqueous mixture and aqueous concentrations of Al, Ba, Ca, Cu, Hg, Sr, and Zn. However, hardening also increased initial aqueous concentrations of B, Cr, K, Mo, Na, P, Sb, Se, Si, and SO_4^{-2}. As weathering progressed, aqueous concentrations of leached elements were similar in hardened versus non-hardened bottom ash indicating that hardening had a greater influence during the initial stages of weathering. Trace elements had minimal aqueous concentration, from both ashes, because of a high pH environment and likely adsorption to secondary minerals. Comparison of aqueous concentrations to aquatic criteria (only for perspective) revealed that Cr, Cu, and Hg initially exceeded some aquatic limits, but concentrations then declined quickly. Only aqueous concentrations of Cl^{-1}, NO_3^{-1}, and NO_2^{-1} in bottom ash and hardened bottom ash leachate exceeded select aquatic criteria over the long-term. The addition of ash to soil (both hardened and non-hardened additions) and subsequent weathering revealed an initial elevation of aqueous As, Al, Ca, Cr, Hg, K, Mg, Mo, Na, P, Si, Sr, and SO_4^{-2} compared to the soil-only treatment. All aqueous concentrations from ash-soil mixes that were elevated compared to the soil-only were eventually similar to soil-only aqueous concentrations over time except As, Mg, P, and Ca. The elevated aqueous concentration of As, Mg, and P may have been due to a lower pH environment compared to ash-only; aqueous As concentrations were still well below limits for aquatic life criteria. As a soil amendment the high pH and low reactivity of both bottom ash and hardened

bottom ash were ideal, and its composition did not exceed any allowable limits set out by SACoP. However, the solubility of components in ash may alter if the pH of the surrounding environment were to become acidic.

3.0 pH Dependent Leaching of Bottom and Hardened Bottom Ash

3.1 INTRODUCTION

The common management practice for ash produced through thermochemical processes is landfilling. Since ash is very alkaline in nature, natural weathering would allow for the pH to gradually decline as the ash reacts within the environment; this provides a steady release of the elements that make up ash. Generally, trace elements are also locked within the ash due to the high pH of ash (Chapter 2). However, this release of elements may be changed if the pH were to decrease, as the dissolution of constituents could be influenced by a more acidic environment. Factors that may lower the pH in environments where ash is stockpiled or stored include acid rain, carbon dioxide contact, and/or acid producing reactions from waste material or organic matter (Fallman and Aurell, 1996). Carbonic acid can be generated from carbon dioxide during the decomposition of organic matter in landfills. This carbonic acid could result in acidic leachates that may come into contact with ash, and in turn influence the composition of ash leachates. Additionally, ash may be used to neutralize acidic mine tailings, but there is a risk that the lowered pH, of the neutralized ash, may release ash components (i.e. metals) into the environment.

Acidity is not the only factor to influence the constituents released from ash but is a primary concern when disposing of ash (Dijkstra et al., 2006; Meima and Comans, 1997, 1998, 1999, and 2002). Other factors include contact time, temperature, mineralogy, redox potential, the amount of liquid to solid contact, and biological activity (Dijkstra et al., 2006; Van der Sloot et al., 1996; Whalstrom, 1996). A better understanding of elemental release from ash may require that some of these factors be controlled during weathering experiments. pH is a key factor that dictates the release of elements during long-term weathering (Dijkstra et al., 2006; Van der Sloot et al., 1996; Vitkova et al., 2009; Whalstrom, 1996).

The leaching behaviour of ashes can be further characterized, apart from sequential batch extraction or column studies, by determining elemental mobility through pH dependency of single batch extracts, known as pH static experimentation (Dijkstra et al., 2006; Whalstrom, 1996). As pH is lowered many of the constituents that make up ash will likely vary in their solubility (Dijkstra et al., 2006; Van der Sloot et al., 1996; Whalstrom, 1996; Meima and Comans, 2002). To gain a more thorough understanding of the leaching behaviour of bottom and hardened bottom ash (in addition to the discoveries made through serial batch extractions in Chapter 2), pH was altered to determine the changes in aqueous phase concentrations of major (Al, Ca, Fe, K, Mg, Mn, Na, P, and Si) and minor elements (As, B, Ba, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Se, Sr, and Zn) as determined by ICP-MS (major and minor elements as defined in Chapter 2).

3.2 METHODOLOGY

3.2.1 Preparation of Bottom and Hardened Bottom Ash

Bottom ash and hardened bottom ash used in the pH static experiment were the same as those used in Chapter 2. All preparations and analyses of the solid phase were described in Chapter 2.

3.2.2 pH Static Experiment

Bottom ash and hardened bottom ash were subjected to the pH static method following the protocol of Van der Sloot et al. (1996) and Wahlstrom (1996). Nalgene centrifuge tubes would degrade rapidly therefore 400mL glass beakers were used; they were acid washed and rinsed with double deionized water after each run. Bottom ash (20.0g OD equivalent, measured to the nearest 0.0001g) was added to a 400mL glass beaker, to which was also added 100mL of double deionized water (L/S 5). Polyether ether ketone, PEEK, stir bars were used to suspend the ash. Nitric acid (1M) was then used to acidify the ash-water mixture and pH was monitored by an

electronic pH meter (Thermo Orion 420A+ Meter). The pH was held at pH 10 for 24 hours. Blanks were run without ash in 400mL glass beakers; these contained 100mL of double deionized water, 1M nitric acid and PEEK stir bar. After 24 hours, all the samples were vacuum filtered through 0.45μm Whatman filter papers using Nalgene filter-ware. Blanks were run simultaneously with the pH static experiment for QA/QC, and revealed only trace amounts of the analyzed elements to be present within the aqueous phase of the blanks (Appendix B2, Table B2.4). The aqueous extract was then analyzed for electrical conductivity (YSI Conductivity Instrument) and oxidation reduction potential (Thermo ORION 3 STAR pH Benchtop Meter). The entire procedure was repeated in quadruplicate for pH 9, 8, 7, 6, 5, and 4 for both bottom and hardened bottom ash. Although target pH was closely achieved for pH 10 to 4 for each sample, the actual pH of the ash-water mixture would vary slightly, but would always be close to the target pH.

Elemental analysis of the extracts was performed by the UNBC Central Equipment Laboratory (CEL) using ICP-MS (Agilent Technologies 7500 Series ICP-MS) for Al, Ba, Ca, Fe, K, Mg, Na, P, Si, As, B, Bi, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Se, Sr, Zn, Ag, Be, Bi, Li, Sb, Sn, Ti, Tl, U, V, W, Y, and Zr; the analysis encompassed all speciations for each element as a total.

3.3 RESULTS

3.3.1 Electrical Conductivity of Aqueous Extracts

Electrical conductivity increased as pH was lowered (Figure 3.0). At pH 4 to 7 aqueous extracts from bottom ash had a lower electrical conductivity than extracts from hardened bottom ash. But, at pH 7 to 10, aqueous extracts from bottom ash had a higher electrical conductivity than those from hardened bottom ash (Figure 3.0). During the pH static experiment, ionic

strength was not controlled; rather only a titration of the material was performed using 1M nitric acid.

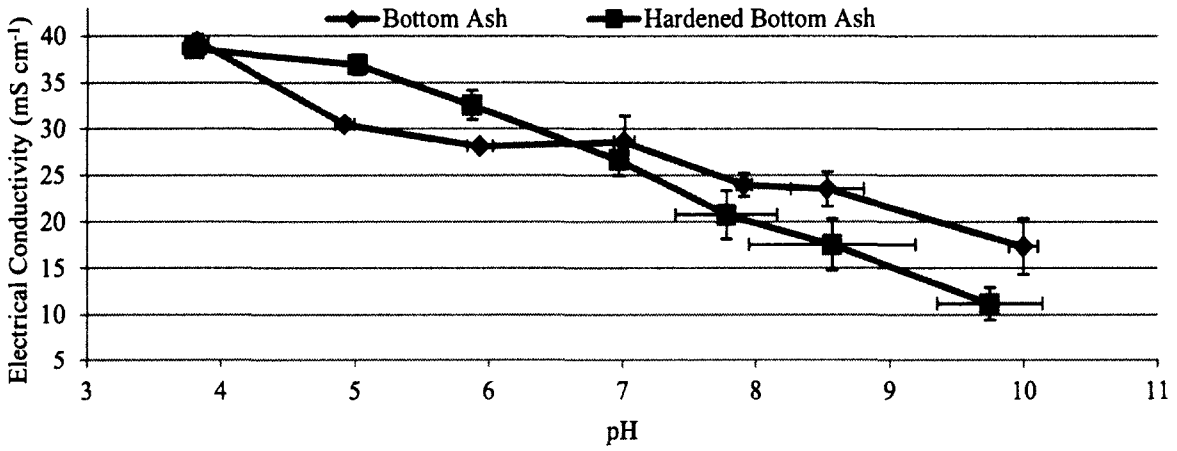

Figure 3.0 - Electrical conductivity results (mS cm^{-1}) for aqueous extracts from bottom and hardened bottom ash ranging from pH 4 to 10 from pH static experiment; n=4.

3.3.2 Aqueous Concentration of Major Elements Versus pH

Most of the major inorganic elements exhibited an increase in aqueous concentration as pH declined. Major inorganic elements that displayed increasing concentrations as pH declined (from 10 to 4) were Ca, Mg, Mn, and Si (Figures 3.2, 3.5, 3.6, and 3.9). Sodium and K showed increases in aqueous concentration as pH declined for bottom ash extracts, but not as prominent as the previous mentioned elements (Figures 3.4 and 3.7). However, acidification of hardened bottom ash produced little change in aqueous concentrations of Na and K as pH declined (Figures 3.7 and 3.4). Additionally, compared to bottom ash leachates, leachates from hardened bottom ash were found to contain higher aqueous concentrations of Na and K from pH 10 to about pH 7 (Figures 3.7 and 3.4). Iron had low leaching as pH varied, and overall a slightly increased concentration as pH decreased (Figure 3.3). Phosphorus was found to have increased aqueous concentrations as pH declined from pH 8 to 6, and then a rapid decline in concentration as pH dropped from pH 6 to 4 (Figure 3.8). Overall, hardening reduced the aqueous concentrations of Ca, Fe, Mn, and P, but increased the aqueous concentration of Na and K.

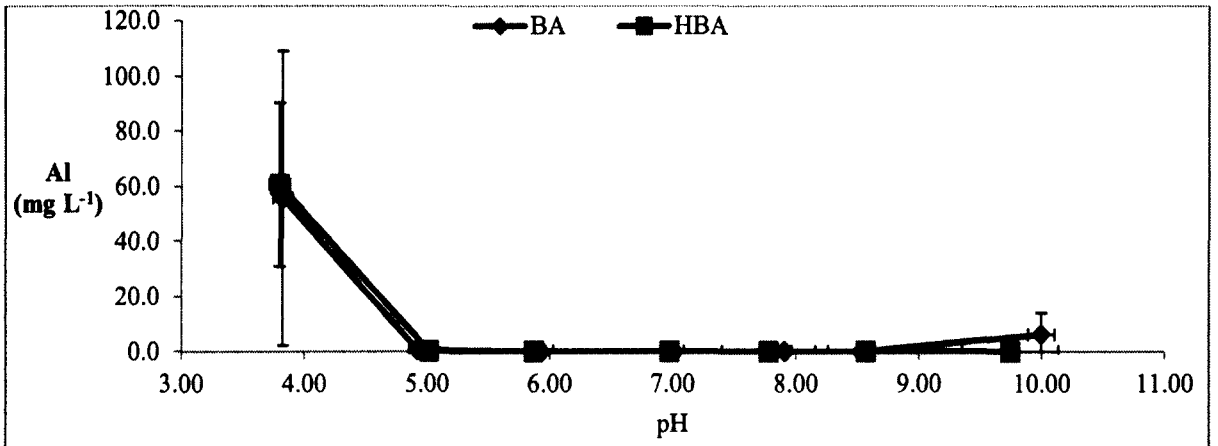

Figure 3.1 - Leaching profile for bottom ash (BA) and hardened bottom ash (HBA) showing aluminum, Al, concentration (mg/L) changes against pH (standard deviation error bars); n=4.

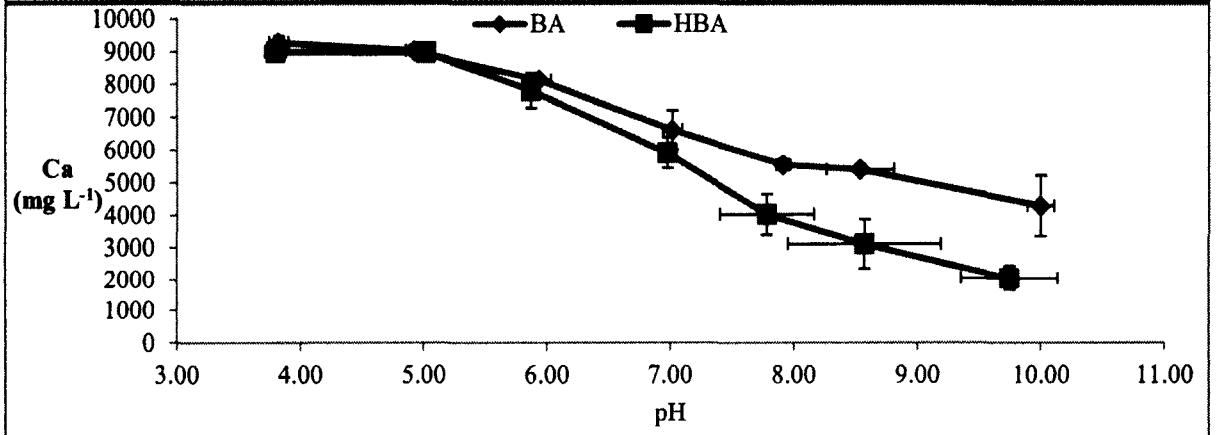

Figure 3.2 - Leaching profile for bottom ash (BA) and hardened bottom ash (HBA) showing calcium, Ca, concentration (mg/L) changes against pH (standard deviation error bars); n=4.

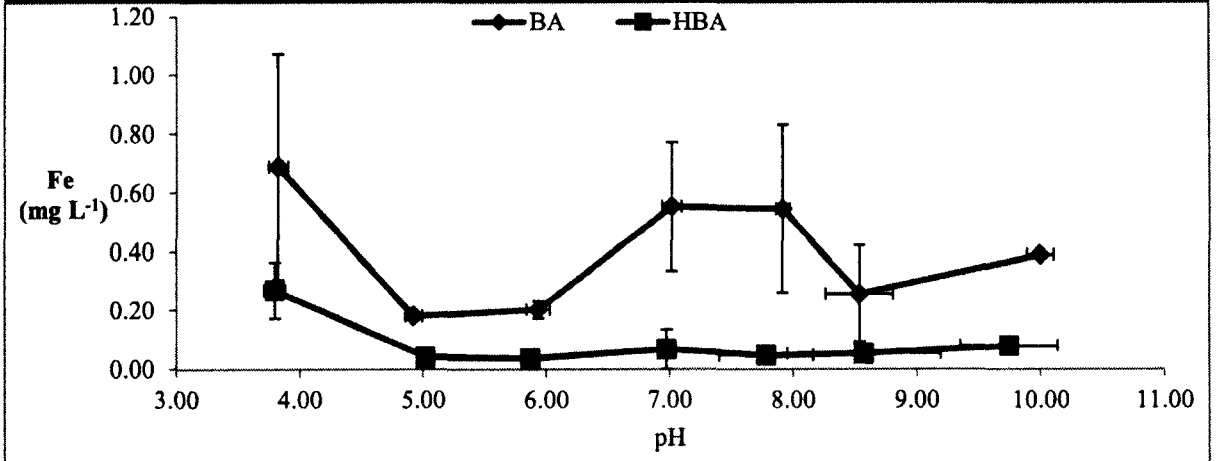

Figure 3.3 - Leaching profile for bottom ash (BA) and hardened bottom ash (HBA) showing iron, Fe, concentration (mg/L) changes against pH (standard deviation error bars); n=4.

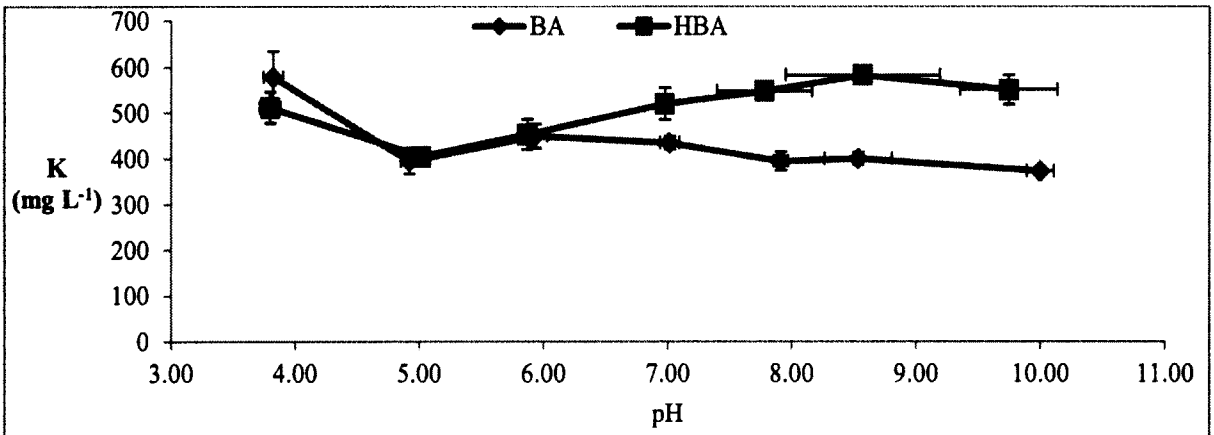

Figure 3.4 - Leaching profile for bottom ash (BA) and hardened bottom ash (HBA) showing potassium, K, concentration (mg/L) changes against pH (standard deviation error bars); n=4.

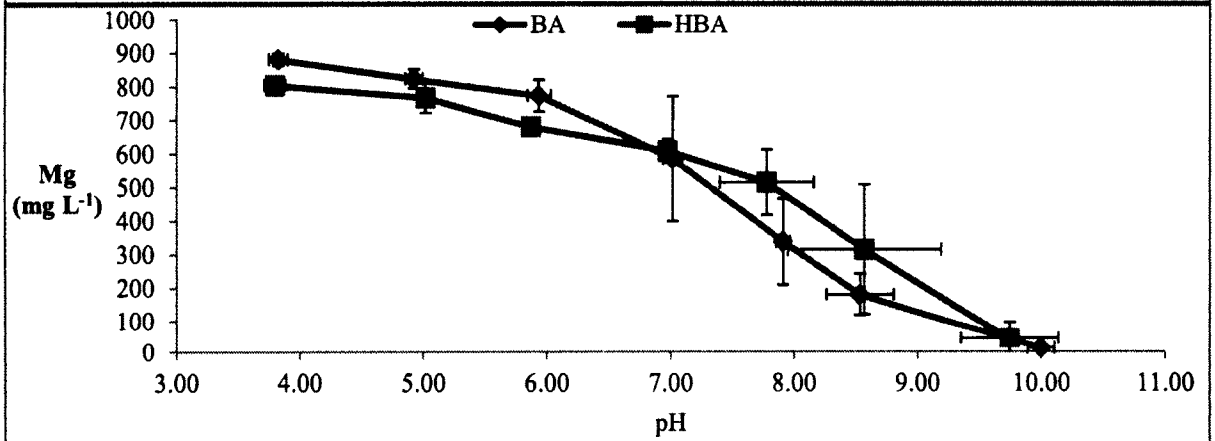

Figure 3.5 - Leaching profile for bottom ash (BA) and hardened bottom ash (HBA) showing magnesium, Mg, concentration (mg/L) changes against pH (standard deviation error bars); n=4.

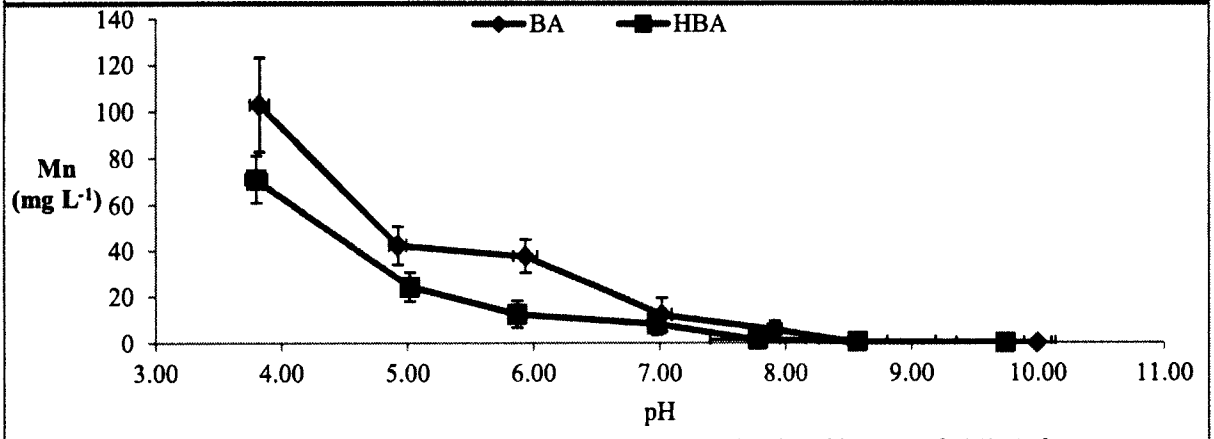

Figure 3.6 - Leaching profile for bottom ash (BA) and hardened bottom ash (HBA) showing manganese, Mn, concentration (mg/L) changes against pH (standard deviation error bars); n=4.

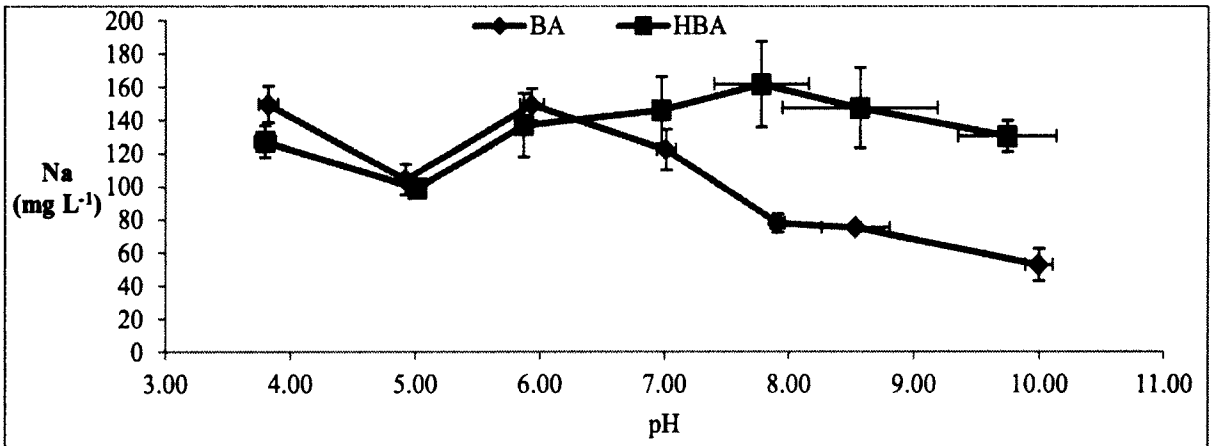

Figure 3.7 - Leaching profile for bottom ash (BA) and hardened bottom ash (HBA) showing sodium, Na, concentration (mg/L) changes against pH (standard deviation error bars); n=4.

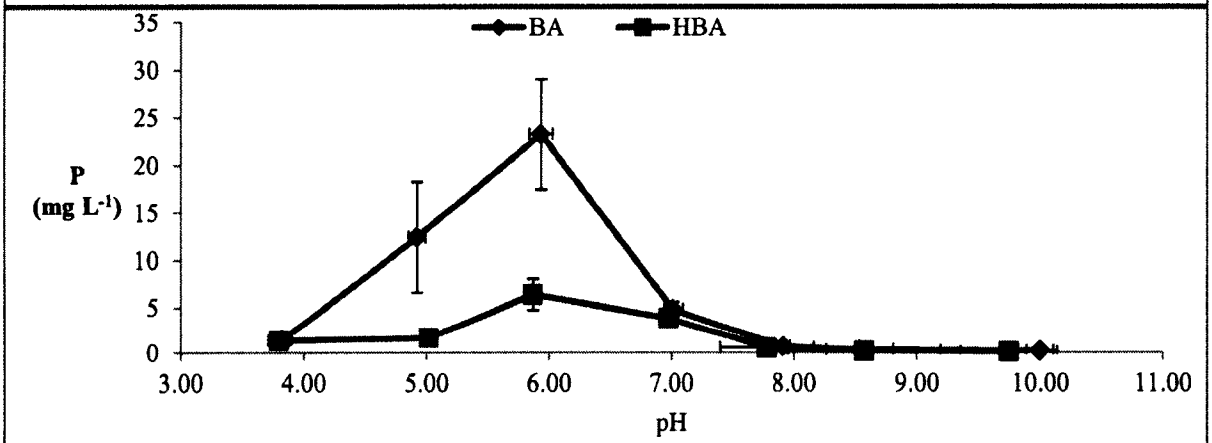

Figure 3.8 - Leaching profile for bottom ash (BA) and hardened bottom ash (HBA) showing phosphorus, P, concentration (mg/L) changes against pH (standard deviation error bars); n=4.

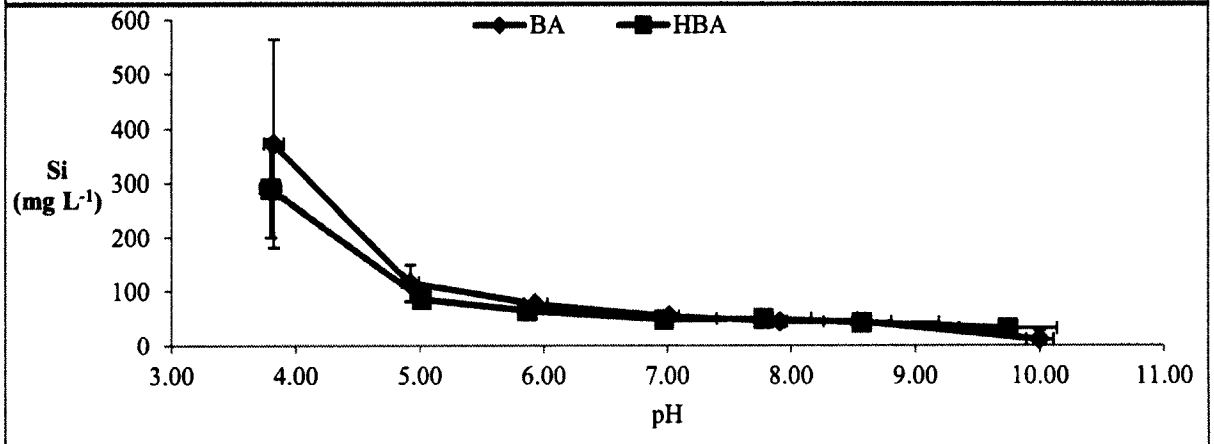

Figure 3.9 - Leaching profile for bottom ash (BA) and hardened bottom ash (HBA) showing silicon, Si, concentration (mg/L) changes against pH (standard deviation error bars); n=4.

3.3.3 Aqueous Concentration of Minor Elements Versus pH

The minor elements that displayed increasing aqueous concentrations as pH was decreased (from 10 to 4) were B, Ba, Cd, Co, Cu, Ni, Sr, and Zn (Figures 3.11, 3.12, 3.13, 3.14, 3.16, 3.19, 3.22, and 3.23). The minor elements that displayed decreased concentrations as pH declined (from 10 to 4) were Cr, Hg, Mo, and Pb (Figures 3.15, 3.17, 3.18, and 3.20). Selenium concentrations stayed relatively constant as pH was varied (Figure 3.21). Aqueous concentrations of As showed enhanced leaching around neutral pH (pH 7 to 5) for both ash treatments (Figure 3.10). Due to hardening, aqueous concentrations of As, Cd, Co, Hg, Ni, and Pb were reduced compared to leachates from non-hardened bottom ash.

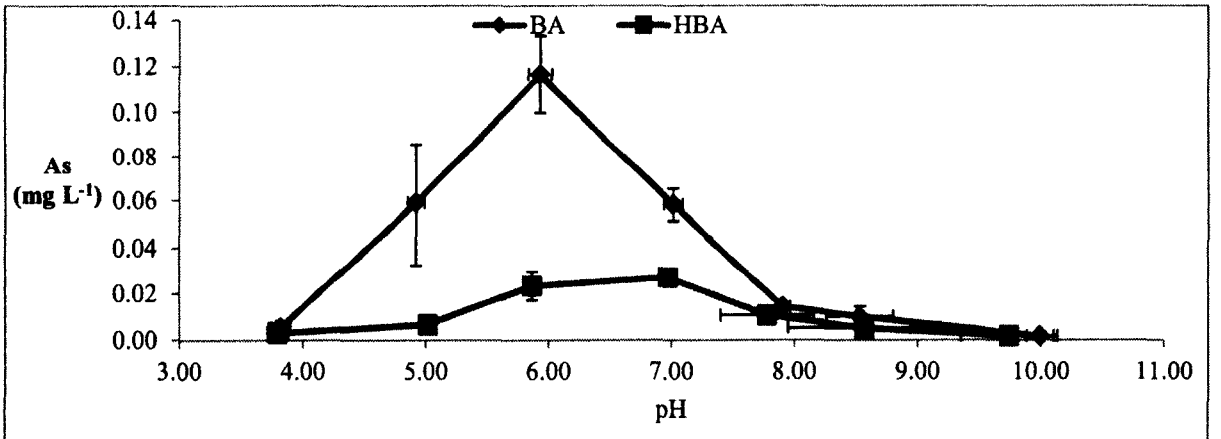

Figure 3.10 - Leaching profile for bottom ash (BA) and hardened bottom ash (HBA) showing arsenic, As, concentration (mg/L) changes against pH (standard deviation error bars); n=4.

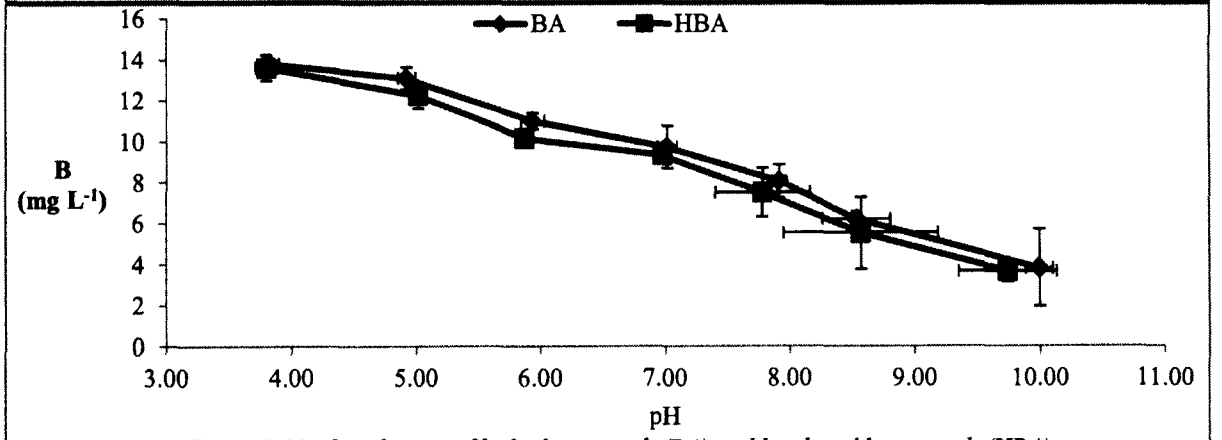

Figure 3.11 - Leaching profile for bottom ash (BA) and hardened bottom ash (HBA) showing boron, B, concentration (mg/L) changes against pH (standard deviation error bars); n=4.

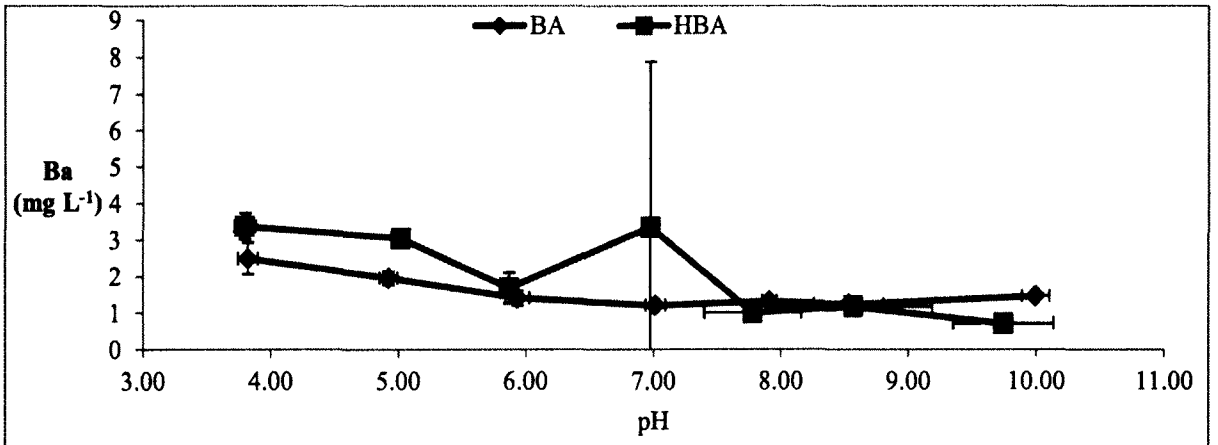

Figure 3.12 - Leaching profile for bottom ash (BA) and hardened bottom ash (HBA) showing barium, Ba, concentration (mg/L) changes against pH (standard deviation error bars); n=4.

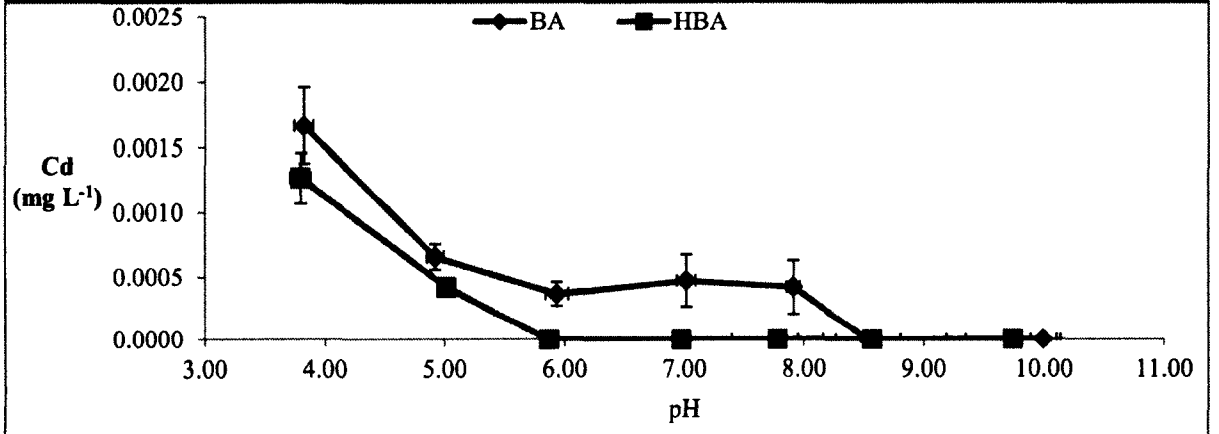

Figure 3.13 - Leaching profile for bottom ash (BA) and hardened bottom ash (HBA) showing cadmium, Cd, concentration (mg/L) changes against pH (standard deviation error bars); n=4.

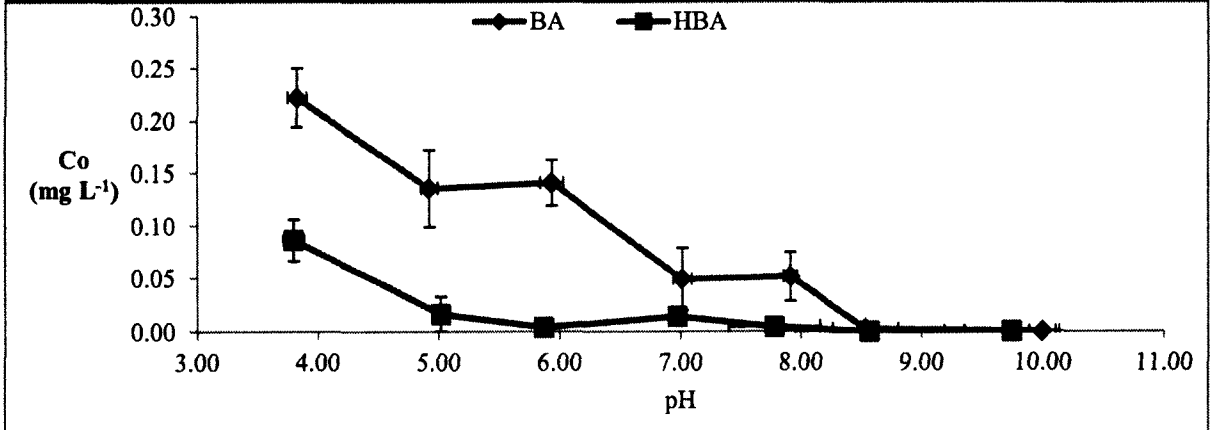

Figure 3.14 - Leaching profile for bottom ash (BA) and hardened bottom ash (HBA) showing cobalt, Co, concentration (mg/L) changes against pH (standard deviation error bars); n=4.

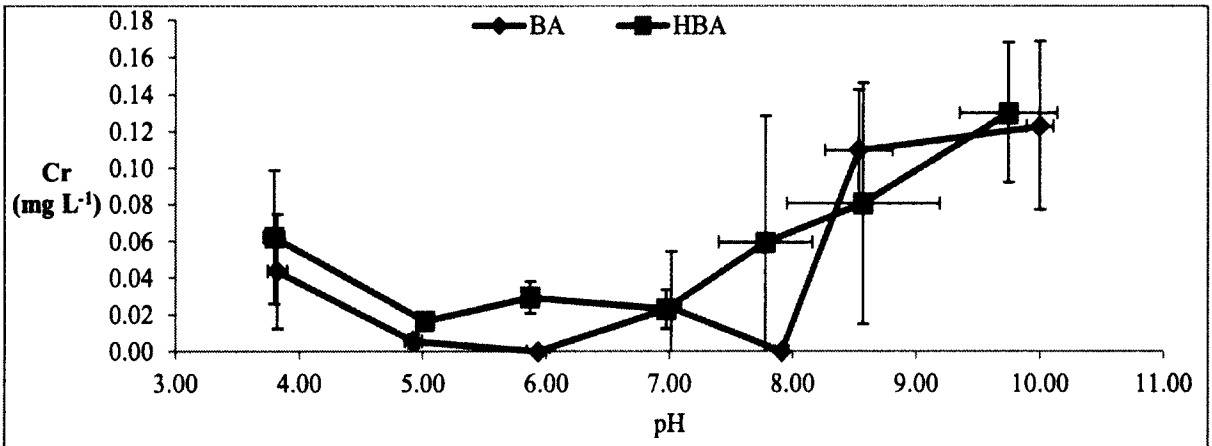

Figure 3.15 - Leaching profile for bottom ash (BA) and hardened bottom ash (HBA) showing chromium, Cr, concentration (mg/L) changes against pH (standard deviation error bars); n=4.

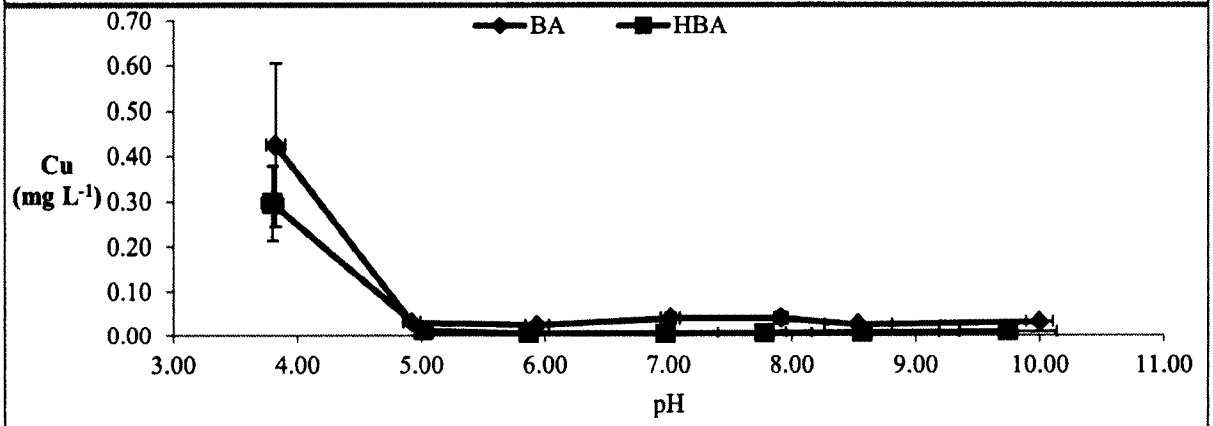

Figure 3.16 - Leaching profile for bottom ash (BA) and hardened bottom ash (HBA) showing copper, Cu, concentration (mg/L) changes against pH (standard deviation error bars); n=4.

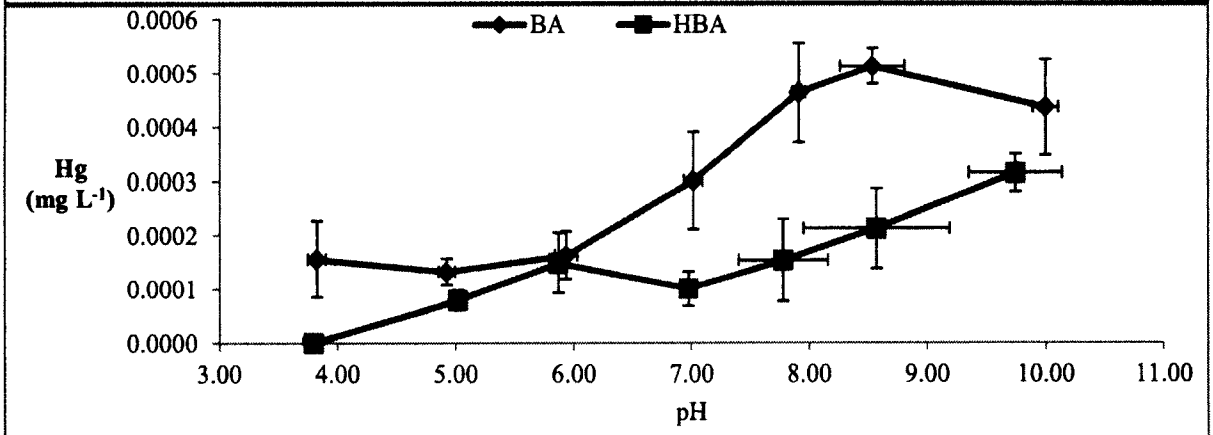

Figure 3.17 - Leaching profile for bottom ash (BA) and hardened bottom ash (HBA) showing mercury, Hg, concentration (mg/L) changes against pH (standard deviation error bars); n=4.

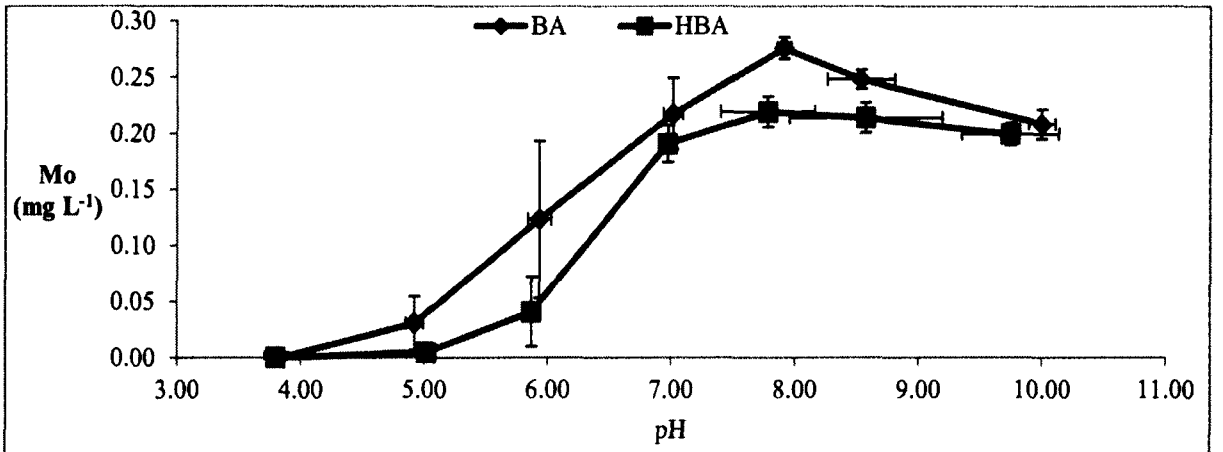

Figure 3.18 - Leaching profile for bottom ash (BA) and hardened bottom ash (HBA) showing molybdenum, Mo, concentration (mg/L) changes against pH (standard deviation error bars); n=4.

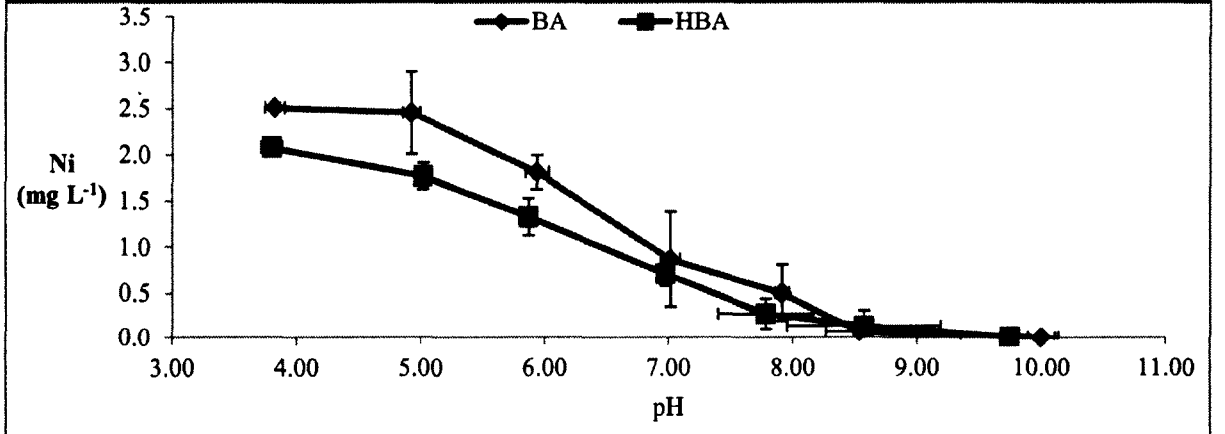

Figure 3.19 - Leaching profile for bottom ash (BA) and hardened bottom ash (HBA) showing nickel, Ni, concentration (mg/L) changes against pH (standard deviation error bars); n=4.

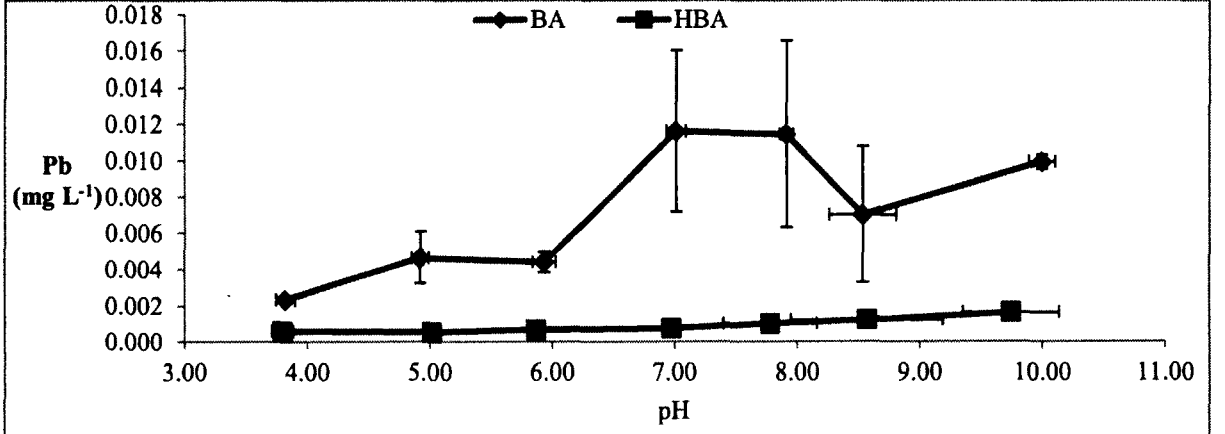

Figure 3.20 - Leaching profile for bottom ash (BA) and hardened bottom ash (HBA) showing lead, Pb, concentration (mg/L) changes against pH (standard deviation error bars); n=4.

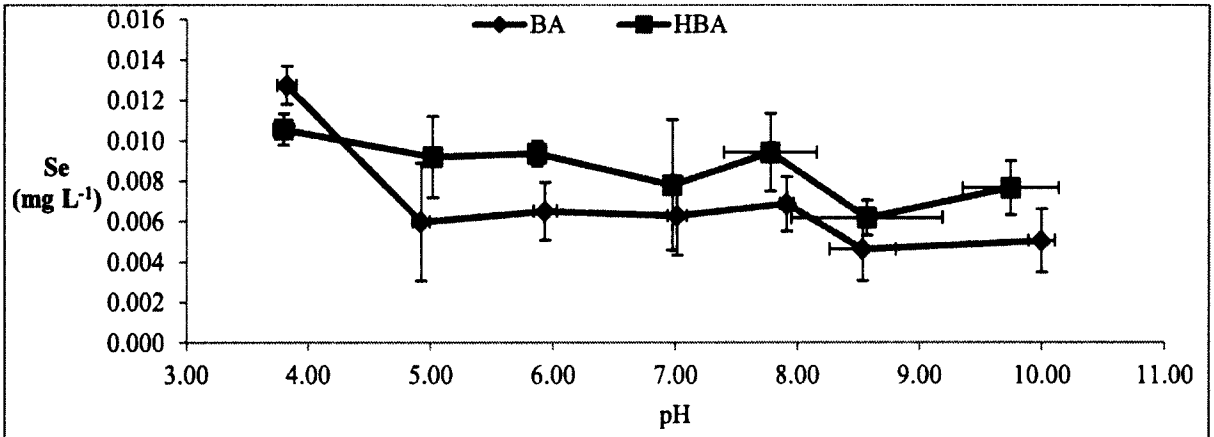

Figure 3.21 - Leaching profile for bottom ash (BA) and hardened bottom ash (HBA) showing selenium, Se, concentration (mg/L) changes against pH (standard deviation error bars); n=4.

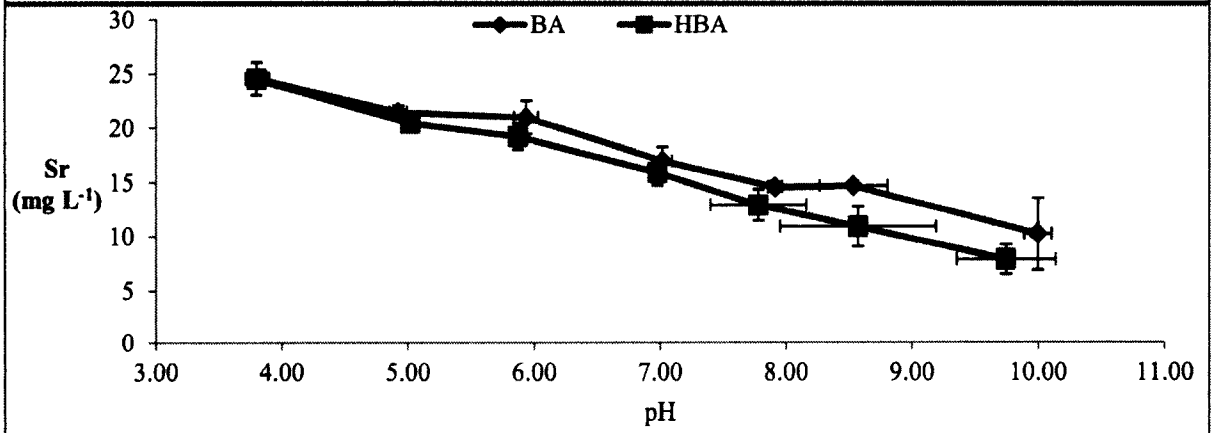

Figure 3.22 - Leaching profile for bottom ash (BA) and hardened bottom ash (HBA) showing strontium, Sr, concentration (mg/L) changes against pH (standard deviation error bars); n=4.

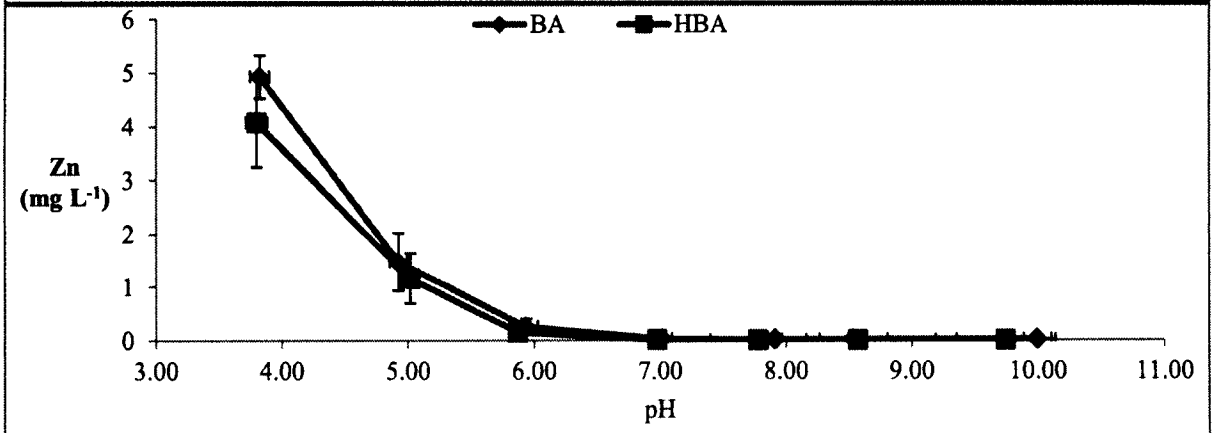

Figure 3.23 - Leaching profile for bottom ash (BA) and hardened bottom ash (HBA) showing zinc, Zn, concentration (mg/L) changes against pH (standard deviation error bars); n=4.

3.3.4 Percent Loss for Individual Elements Leached from Ash into the Aqueous Phase

Percent loss for the elements was calculated by determining the total amount present in the aqueous phase (i.e. ICP data of the aqueous phase and the total volume used during extraction) and dividing that by the total amount available in the solid material (i.e. ICP data of the solid phase and total solid material used during extraction). A sample calculation can be found in the Appendix B2.

The maximum percent loss for many of the major inorganic elements contained in BA or HBA normally occurred at the lowest pH (Table 3.0 and 3.1). Maximum leaching for Al, B, Ba, Ca, Fe, K (in BA), Mg, Mn, Na (in BA), and Sr in BA and HBA occurred at pH 4. Similarly, minimum leaching of these mentioned elements occurred at highest pH (pH 10). Maximum leaching for K (in HBA) and Na (in HBA) did not change drastically as pH was altered (Table 3.0 and Table 3.1). Finally, the amount of P leached was at a maximum at pH 6 for both BA and HBA, whereas a minimum was observed at high pH (Table 3.0 and 3.1).

Similar to the major inorganic elements leached, the maximum percent loss of many of the minor elements leached from BA and HBA also occurred at the lowest pH (Table 3.0 and 3.1). Maximum leaching for Cd, Co, Cu, Ni, and Zn occurred at approximately pH 4 (Table 3.0 and 3.1). Maximum leaching for Cr, Hg, and Mo occurred at high pH for both BA and HBA (approximately pH 9 to 10) (Table 3.0 and 3.1). Lead leaching was at a maximum approximately pH 7 for BA (Table 3.0) and pH 10 for HBA (Table 3.1). Arsenic leaching was at a maximum at pH 6 for both BA and HBA (Table 3.0 and 3.1).

Table 3.0 – Percent loss for elements leached from bottom ash based on original solid phase concentrations (from HNO_3/HCl digest) and amount of ash used during pH static experiment for pH 10 to 4.

Parameter	pH 10		pH 9		pH8		pH 7		pH 6		pH 5		pH 4	
	Mean	*SD*	*Mean*	*SD*	*Mean*	*SD*	*Mean*	*SD*	*Mean*	*SD*	*Mean*	*SD*	*Mean*	*SD*
Ag (%)**	0.27	0.14	0.27	0.15	0.43	0.20	0.33	0.14	0.32	0.15	0.33	0.12	0.33	0.19
Al (%)	0.22	0.28	0.002	0.001	0.004	0.002	0.005	0.001	0.006	0.001	0.05	0.06	3.58	3.48
As (%)	0.19	0.13	1.16	0.50	1.71	0.16	7.81	1.41	18.3	2.8	9.86	4.30	0.97	0.49
B (%)	17.7	9.5	30.7	2.2	41.3	4.9	55.6	8.8	73.8	3.6	93.4	5.4	107	2
Ba (%)	0.69	0.06	0.64	0.01	0.70	0.04	0.72	0.03	0.99	0.15	1.46	0.15	2.01	0.38
Ca (%)	24.3	6.6	33.2	1.2	35.3	1.7	47.0	7.1	68.1	1.8	80.3	2.4	89.3	2.5
Cd (%)**	n/a	n/a	n/a	n/a	0.60	0.30	0.76	0.35	0.69	0.17	1.31	0.17	3.61	0.68
Co (%)	n/a	n/a	0.09	0.06	2.03	0.95	2.20	1.37	7.28	1.21	7.41	1.92	13.2	1.8
Cr (%)	2.12	0.86	2.04	0.60	n/a	n/a	0.49	0.59	n/a	n/a	0.15	0.10	1.28	0.94
Cu (%)	0.44	0.04	0.39	0.13	0.62	0.19	0.70	0.24	0.50	0.06	0.68	0.18	9.65	4.26
Fe (%)	0.016	0.001	0.012	0.008	0.025	0.013	0.029	0.012	0.012	0.002	0.0117	0.0005	0.049	0.028
Hg (%)**	0.28	0.07	0.35	0.02	0.33	0.06	0.24	0.05	0.15	0.04	0.13	0.03	0.17	0.07
K (%)	12.0	0.9	14.0	0.6	14.3	0.7	17.5	1.2	21.4	1.5	20.0	1.8	31.7	3.5
Li (%)	0.59	0.29	1.49	0.31	2.33	0.49	4.43	1.28	7.63	1.16	8.29	0.84	12.5	1.1
Mg (%)	0.63	0.56	9.25	3.22	18.0	7.2	35.1	12.6	54.1	4.1	61.2	3.3	70.8	2.1
Mn (%)	0.002	0.001	0.05	0.04	0.64	0.40	1.51	0.93	5.36	1.11	6.43	1.37	16.9	3.6
Mo (%)	22.5	2.1	29.3	1.1	33.7	1.9	29.4	3.0	19.7	10.9	5.16	3.92	n/a	n/a
Na (%)	7.89	1.85	12.2	0.6	13.1	0.9	22.9	3.2	33.1	2.5	24.5	2.7	38.1	3.3
Ni (%)	0.02	0.01	0.78	0.50	5.90	3.78	11.6	7.1	27.9	3.3	40.2	7.7	44.5	1.5
P (%)	0.02	0.004	0.04	0.02	0.09	0.03	0.68	0.13	3.86	1.00	2.19	1.00	0.29	0.15
Pb (%)**	6.25	0.36	4.85	2.64	8.18	3.70	9.37	3.85	4.14	0.55	4.64	1.42	2.51	0.13
Sb (%)**	1.64	0.49	3.23	0.59	3.93	0.78	5.97	1.91	7.92	2.81	6.24	2.06	6.22	3.33
Sn (%)	3.06	0.22	2.23	1.51	7.40	4.19	8.39	3.64	4.32	0.49	5.15	0.18	1.99	0.27
Sr (%)	15.0	5.6	23.2	0.9	23.9	1.1	31.1	4.2	45.3	4.0	49.3	2.2	60.9	2.8
Ti (%)	n/a	n/a	0.001	0.001	0.002	0.001	0.003	0.001	0.003	0.001	0.004	0.003	0.011	0.006
Tl (%)**	0.79	0.61	0.24	0.12	0.73	0.41	0.22	0.16	n/a	n/a	0.23	0.08	n/a	n/a
U (%)**	0.01	0.003	0.03	0.02	0.07	0.02	0.11	0.03	0.05	0.03	0.01	0.00	0.01	0.01
V (%)	0.34	0.34	0.81	0.05	0.53	0.05	1.61	0.57	1.96	0.15	0.68	0.20	0.18	0.04
Y (%)**	0.07	0.02	0.08	0.02	0.11	0.04	0.18	0.03	0.17	0.05	0.65	0.36	48.3	22.4
Zn (%)	0.07	0.01	0.06	0.01	0.07	0.01	0.14	0.05	1.63	0.94	10.0	3.8	36.1	3.4
Zr (%)	0.01	0.001	0.01	0.00	0.01	0.00	0.01	0.00	n/a	n/a	0.01	0.00	0.02	0.01

**n/a designation is given for undetected, **Estimation based on detection limit, ***Be and Bi were undetected*

Table 3.1 – Percent loss for elements leached from hardened bottom ash based on original solid phase concentrations (from HNO_3/HCl digest) and amount of ash used during pH static experiment for pH 10 to 4.

Parameter	pH 10		pH 9		pH8		pH 7		pH 6		pH 5		pH 4	
	Mean	*SD*	*Mean*	*SD*	*Mean*	*SD*	*Mean*	*SD*	*Mean*	*SD*	*Mean*	*SD*	*Mean*	*SD*
Ag (%)**	0.11	0.04	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.37	0.17
Al (%)	0.001	0.001	0.0008	0.0005	0.0007	0.0002	0.003	0.003	0.0021	0.0002	0.01	0.01	3.86	1.88
As (%)	0.15	0.11	0.47	0.25	1.01	0.14	2.97	0.17	3.06	0.68	0.96	0.34	0.46	0.08
B (%)	17.4	2.9	29.1	11.4	42.3	8.6	59.4	4.1	77.5	5.0	103	6	119	7
Ba (%)	0.32	0.04	0.58	0.09	0.54	0.07	1.98	2.60	1.24	0.37	2.46	0.17	2.83	0.33
Ca (%)	11.7	2.5	19.6	6.3	27.2	5.5	45.2	5.2	71.7	8.3	91.0	3.8	94.6	2.7
Cd (%)**	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.85	0.14	2.65	0.39
Co (%)	n/a	n/a	n/a	n/a	0.18	0.14	0.66	0.41	0.22	0.18	1.03	1.06	5.60	1.32
Cr (%)	2.04	0.63	1.33	1.05	1.06	1.19	0.48	0.20	0.74	0.21	0.46	0.09	1.80	1.04
Cu (%)	0.12	0.01	0.09	0.005	0.08	0.01	0.09	0.03	0.11	0.03	0.30	0.10	7.04	1.97
Fe (%)	0.0027	0.0003	0.002	0.0002	0.0019	0.0004	0.003	0.003	0.002	0.0002	0.0026	0.0005	0.017	0.006
Hg (%)**	0.18	0.02	0.13	0.04	0.10	0.05	0.08	0.02	0.14	0.05	0.08	0.02	n/a	n/a
K (%)	16.1	1.0	18.7	1.4	19.0	0.9	20.4	1.5	21.4	1.7	21.1	1.0	27.7	2.0
Li (%)	0.80	0.24	2.35	1.40	3.49	0.93	4.42	0.58	6.11	0.82	7.03	0.49	10.1	1.0
Mg (%)	2.04	2.44	16.0	10.7	27.71	6.50	36.9	3.1	49.7	4.3	61.9	4.8	67.4	1.2
Mn (%)	0.00	0.00	0.06	0.12	0.18	0.27	1.10	0.66	1.97	0.97	4.22	1.18	12.8	2.0
Mo (%)	19.6	1.2	23.0	1.9	25.4	1.0	25.1	1.7	6.28	4.53	0.85	0.25	n/a	n/a
Na (%)	17.2	1.4	21.4	4.7	25.3	4.8	25.9	3.7	29.1	3.4	23.2	1.0	31.1	2.7
Ni (%)	0.09	0.05	1.58	2.18	3.31	2.18	9.69	2.05	21.8	4.2	32.1	3.2	39.1	1.7
P (%)	0.01	0.01	0.03	0.03	0.08	0.01	0.59	0.09	1.16	0.25	0.34	0.14	0.30	0.21
Pb (%)**	0.92	0.04	0.75	0.17	0.67	0.14	0.56	0.22	0.60	0.08	0.52	0.04	0.60	0.16
Sb (%)**	1.60	0.34	3.20	1.51	4.63	1.28	7.77	0.99	8.11	0.72	4.61	0.38	3.75	1.12
Sn (%)	1.74	0.13	0.95	0.10	1.06	0.08	0.84	0.41	1.05	0.15	1.07	0.28	0.83	0.16
Sr (%)	11.1	2.2	16.9	4.1	21.5	3.5	30.0	3.2	43.6	4.7	51.3	3.2	63.9	4.6
Ti (%)	0.0010	0.0009	0.0006	0.0003	0.0007	0.0003	0.0027	0.0029	0.0013	0.0006	0.0015	0.0007	0.004	0.003
Tl (%)**	n/a	n/a	n/a	n/a	0.23	0.10	n/a	n/a	0.65	0.39	n/a	n/a	n/a	n/a
U (%)**	n/a	n/a	0.02	0.02	0.05	0.02	0.13	0.02	0.05	0.05	n/a	n/a	0.01	0.01
V (%)	0.48	0.06	0.42	0.09	0.34	0.05	0.60	0.10	0.31	0.13	0.11	0.03	0.06	0.01
Y (%)**	n/a	n/a	n/a	n/a	n/a	n/a	0.20	0.15	0.15	0.04	1.53	1.11	49.4	17.2
Zn (%)	0.03	0.00	0.03	0.01	0.03	0.01	0.10	0.03	1.54	0.89	12.6	5.4	45.7	9.8

**n/a designation is given for undetected, **Estimation based on detection limit, ***Be, Bi, and Zr were undetected*

3.3.5 Aqueous Ion Concentrations Compared to Aquatic Criteria

The British Columbia Contaminated Sites Regulation (BCCSR) has maximum allowable limits set for the aqueous concentrations of major inorganic elements Al, Fe, Mg, Mn, and Na for different water types (Freshwater Aquatic Life, Marine Water Aquatic Life, and Drinking Water); (Table 3.2). Minor elements monitored are those of As, B, Ba, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Se and Zn (Table 3.2). The values presented in Table 3.2 are intended to put the maximum concentrations reached during the pH static experiment into perspective as these extracts were never intended for drinking water (Table 3.2).

Both bottom ash and hardened bottom ash treatments exceeded the limits of Al, Mg, and Mn for safe drinking water. Bottom ash and hardened bottom ash treatments exceeded the allowable Al limit at pH 4 (Table 3.2). The safe limit for Mg was exceeded below pH 9 for both ashes. At pH 8 and lower, Mn limits were exceeded for both ashes (Table 3.2).

Bottom ash exceeded the safe drinking water limits of As (116ppb at pH 6), Cr (120ppb at pH 10), Mo (280ppb at pH 8), Pb (11ppb at pH 8), and Se (13ppb at pH4), whereas hardened bottom ash exceeded the safe drinking water limits of As (27ppb at pH 7), Cr (130ppb at pH10), and Se (11ppb at pH 4).

The BCCSR also has allowable limits for elemental concentration for freshwater aquatic life (FAL) and marine aquatic life (MAL). The 50ppb limit for As was exceeded between pH 7 and 5 for the bottom ash treatment, but never exceeded 27ppb for hardened bottom ash at any pH range (Table 3.2). Cadmium limits of 0.1ppb were exceeded by the bottom ash treatment below pH 9, whereas the hardened bottom ash treatment exceeded 0.1ppb below pH 6. Cobalt limits (40ppb) were exceeded below pH 8.5 (maximum 222ppb at pH 4) and below pH 5 (maximum 86ppb at pH 4) for bottom ash and hardened bottom ash respectively (Table 3.2). Chromium limits (10ppb) were also exceeded below pH 5 and at pH 10 for both ashes. Copper limits

(20ppb) were exceeded below pH 5 for both ash treatments. Nickel limits were also exceeded below pH 8.5 for both ash treatments reaching maximum concentrations of 2510ppb (bottom ash treatment) and 2080ppb (hardened bottom ash treatment) at pH 4. Aqueous concentrations of Se only exceeded the 10ppb limit below pH 5, reaching 13ppb (bottom ash treatment at pH 4) and 11ppb (hardened bottom ash treatment at pH 4). Aqueous concentrations of Zn exceeded the BCCSR limit (75ppb) at levels below pH 7, where a maximum of 4930ppb (bottom ash treatment at pH 4) and 4080ppb (hardened bottom ash treatment at pH 4) were reached (Table 3.2).

Table 3.2 – Maximum aqueous concentrations (ppm and ppb as indicated) reached for the major and minor elements from pH static testing (ppm or ppb at determined pH in brackets) compared to aquatic criteria set by British Columbia Contaminated Sites Regulation (BCCSR).

Parameter	BA	HBA	BCCSR		
			FAL	MAL	DW
Al (ppm)	55.76 (pH4)	60.68 (pH4)			9.5
B (ppm)	13.81 (pH4)	13.61 (pH4)	50		
Ba (ppm)	2.5 (pH4)	3.4 (pH4)	10	5	
Fe (ppm)	0.69 (pH4)	0.27 (pH4)			6.5
Mg (ppm)	804 (pH4)	881 (pH4)			100
Mn (ppm)	103 (pH4)	71 (pH4)			0.55
Na (ppm)	150 (pH4)	162 (pH8)			200
As (ppb)	116 (pH6)	27 (pH7)	50	125	10
Cd (ppb)	1.7 (pH4)	1.3 (pH4)	0.1	0.1	5
Co (ppb)	222 (pH4)	86 (pH4)	40		
Cr (ppb)	120 (pH10)	130 (pH10)	10	50	50
Cu (ppb)	300 (pH4)	420 (pH4)	20	20	1000
Hg (ppb)	0.51 (pH9)	0.32 (pH10)	1		1
Mo (ppb)	280 (pH8)	220 (pH8)	10000		250
Ni (ppb)	2510 (pH4)	2080 (pH4)	83		
Pb (ppb)	11 (pH8)	2 (pH10)	40	20	10
Se (ppb)	13 (pH4)	11 (pH4)	10	540	10
Zn (ppb)	4930 (pH4)	4080 (pH4)	75	100	

**Freshwater Aquatic Life (FAL), Marine Water Aquatic Life (MAL), Drinking Water (DW)*

***Aqueous concentrations were shown as a comparison to BCCSR guidelines to provide perspective on maximum observed concentrations*

3.4 DISCUSSION

As found from the long-term weathering of bottom ash, at high pH, leachates were generally dominated by Ca, K, Si, Al, Ba, Na, and SO_4^{-2} while aqueous trace metal content was minimal (Chapter 2). The low aqueous concentrations of trace metals were mainly due to the high pH of the resulting ash-water mixtures. However, the dissolution of minerals from biomass ash can be affected by acidic environments (Dijkstra et al., 2006). As pH is altered many of the constituents (i.e. elemental constituents) that make up ash will exhibit altered solubility; most of which have shown increased mobility at the acidic range (Dijkstra et al., 2006; Vitkova et al., 2009). Acidification during a single batch extraction (i.e. pH static experiment) can be used to study the leaching behaviour of bottom and hardened bottom ash. In this study, pH was altered to determine its effect on the concentrations of elements within the aqueous phase.

3.4.1 pH Static Leaching of Ash – Hardened versus Non-Hardened Ash

To acidify the ash-water mixture 1M nitric acid was used to bring the pH of the ash-water mixture to a specific set point; this required constant addition of acid over a 24hr period as the pH of the ash-water mixture would continually rise. The constant addition of acid to maintain a stable pH indicated a high buffering capacity for bottom ash and hardened bottom ash. The high buffering capacity may be due to the presence of hydroxides and carbonates in both hardened and unhardened bottom ash (Dijkstra et al., 2006). It has been reported that Ca, Mg, and Si bearing minerals control the high buffering capacity of bottom ash (Johnson et al., 1995; Yan et al., 1998). In this study, bottom ash and hardened bottom ash buffering capacities were likely controlled by minerals containing Ca, Mg, K, and Na as these elements showed the highest aqueous concentration at all pH values (Figures 3.2, 3.5, 3.4, 3.7, 3.9, and 3.6). As pH declined, the aqueous concentrations of Ca, Mg, K, Na, Si, and Mn increased, and were accompanied by a high electrical conductivity (Figure 3.0). The high aqueous concentrations of these elements in

bottom ash leachates were consistent with other static leaching studies (Dijkstra et al., 2006; Meima and Comans 1997, 1998, and 1999)

Hardening influenced the leaching of elements from bottom ash during acidification. Hardening reduced the aqueous concentrations of Ca, Fe, Mn, and P as compared to non-hardened ash. In addition, compared to non-hardened bottom ash, the electrical conductivity of the aqueous mixture containing hardened bottom ash was also found to be lower (Figure 3.0). However, below pH 7, the electrical conductivity was observed to have increased over non-hardened bottom ash-water mixtures. At pH 4, electrical conductivity of hardened and non-hardened ash-water mixtures was the same (Figure 3.0).

Some elements exhibited a higher aqueous concentration due to hardening; these elements were K and Na (Figures 3.4 and 3.7). High K and Na aqueous concentrations were observed at high pH, but as pH was reduced (below pH 6), K and Na aqueous concentrations were similar to non-hardened bottom ash. This increase in aqueous K and Na concentration from hardened bottom ash may have been due to K- and Na-chlorides/sulphates present in hardened ash (Meima and Comans, 1997). These salts are highly soluble and would account for the increased aqueous concentration of K and Na at higher pH (Figures 3.4 and 3.7). Hardening also reduced the ability of some trace metals to be leached from bottom ash (As, Cd, Co, Hg, Ni, and Pb). With a concern for these trace elements becoming mobile in ash when acidified and in contact with water, a reduction in dissolution due to hardening is beneficial. Generally, hardening influenced leaching at higher pH (Figure 3.0); but, as pH declined, hardened ash was found to show similar leaching as unhardened bottom ash. Overall, the elements that exhibited an increase in aqueous concentration as a result of acidification were As, B, Ca, Cd, Co, Cu, Mg, Mn, Ni, Si, Sr, and Zn; these were primarily major inorganic elements. Other elements that exhibited a decline in concentration were Cr, Hg, Mo, and Pb for both bottom ash and hardened bottom ash.

The pH-leaching profiles of many elements were similar to findings from other studies (Comans and Middelburg, 1987; Dijkstra et al., 2006; Johnson et al., 1995; Meima and Comans 1997, 1998, and 1999; Quina et al., 2009). A few elements, Ca, K, Na, and Mg can be discussed as to their solubility-controlling minerals found in bottom ashes. At high pH (approximately pH 12 to 10), the solubility-controlling minerals for Ca and Mg are likely portlandite and brucite (Johnson et al., 1995; Meima and Comans, 1997). Portlandite forms as a result of hydrolysis from CaO present in ash (Meima and Comans, 1997). Brucite was also predicted to be the main solubility-controlling mineral for Mg during the weathering of bottom ash (Chapter 2). Below pH 12, portlandite dissolves and gypsum is likely the solubility-controlling mineral for Ca dissolution in bottom ashes (Dijkstra et al., 2006; Meima and Comans, 1997). Potassium and Na leaching may be due to soluble salts of K- and Na-chlorides/sulphates present in bottom ashes (Meima and Comans, 1997). Regardless of pH (even though slight aqueous concentration increases were seen), Na and K were relatively insensitive to the influence of pH (Table 3.0 and 3.1). These were similar to findings by Quina et al. (2009), and may have been be due to K- and Na-chloride/sulphate salts, of which hardened bottom ash may have had more of.

Similar to the major inorganic elements, some leached trace elements were found to increase in aqueous concentration as pH declined; these trace elements were As, Cd, Co, Cu, Ni, and Zn. Some trace elements (Cr, Hg, Mo, and Pb) decreased in aqueous concentration as pH declined. However, trace metal leaching from both ashes was still relatively low compared to the major inorganic elements and only exceeded limits for MAL and FAL aqueous systems when the system became quite acidic (i.e. pH 5 or 4) (Table 3.2). Further data on aqueous concentrations as a result of pH change can be found in Figures 3.1 to 3.23. The allowable limits that were exceeded by trace elements are discussed a little later (Section 3.4.2). Low trace metal leaching may have been due to adsorption to secondary minerals or due to low solubility. Declining

aqueous concentrations for Cr, Hg, Mo, and Pb upon acidification may have been due to the presence and/or formation of Fe- and Al-oxides/hydroxides in ash-water systems. For example, Mo and Pb are easily bound to hydrous ferric oxides and aluminum hydroxides (Meima and Comans, 1998 and 1999). As pH was reduced, Fe and Al aqueous concentrations slightly increased (Figures 3.1 and 3.5), which may have caused a greater likelihood for secondary minerals to form. If there was an increased formation of Fe and Al secondary minerals at lower pH, then that would allow for even more adsorption of aqueous Mo and Pb, and in effect lower their aqueous concentration, as was seen (Figures 3.19 and 3.21). As with the adsorption of Mo and Pb ions in solution to Fe- and Al-oxides/hydroxides, Cr and Hg ions in solution may have undergone the same adsorption as well, as their pH-leaching profiles were similar to Mo and Pb (Figures 3.18 and 3.20).

Increasing aqueous concentrations for As, Cd, Co, Cu, and Zn as pH declined may have been due to general acidification allowing for greater dissolution of minerals at lower pH, but at higher pH their low dissolution may have been in part due to the surface complexation to calcite. For example, Cd, Zn, and Co have a great affinity towards calcite; that is they are readily adsorbed to the surface of calcite (Comans and Middelburg, 1987). Since calcite commonly forms at high pH in ash-water systems (Steenari and Karlsson, 1999) (Chapter 2; Table 2.8 and 2.9), the aqueous concentrations of As, Cd, Co, Cu, and Zn would likely be much lower at higher pH than lower pH due to adsorption to calcite. At lower pH, calcite formation would not be as prominent, allowing for greater As, Cd, Co, Cu, and Zn aqueous concentrations.

3.4.2 Implications of Ash Utilization on Land

The results of this pH static study have implications for storage of ash or utilization of ash as a soil amendment to acidic environments. Ash is normally alkaline and many constituents were relatively immobile under high pH conditions. However, as pH declined the aqueous

concentrations of major inorganic elements B, Ca, Mg, Mn, Si, and Sr, and minor elements As, Cd, Co, Cu, Ni, and Zn increased in aqueous concentration for both ashes. Even though the aqueous concentrations of many elements increased as pH declined, their aqueous concentrations did not exceed most aquatic criteria until pH 4 (Table 3.2). The British Columbia Contaminated Sites Regulation (Schedule 6) has set maximum allowable limits on several elemental concentrations within aqueous systems (See Table 3.2). The focus of this study was to determine how elemental leachability changes due to acidification of bottom ash and hardened bottom ash. The comparison of elemental concentrations contained within the extracts to BCCSR limits were only used to provide perspective to the aqueous concentrations. The aqueous concentrations of many trace elements stayed well below allowable limits (set by BCCSR) for freshwater aquatic life at neutral to high pH (Figures 3.1 to 3.23). It was only at low pH (approximately below pH 5) that the aqueous concentrations of most elements of concern exceeded allowable criteria (Table 3.2).

3.4.3 Concluding Thoughts

Bottom ash and hardened bottom ash had a very high buffering capacity, which was likely controlled by minerals containing Ca, Mg, K, and Na as these elements dominated the aqueous concentration at all pH ranges. The acidification of bottom ash and hardened bottom ash resulted in the increased aqueous concentrations of As, B, Ba, Ca, Cd, Co, Cu, Mg, Mn, Ni, Si, Sr, and Zn, whereas a decrease in aqueous concentration was seen for Cr, Hg, Mo, and Pb. Hardening of bottom ash had the greatest influence at high pH, where Ca, Fe, Mn, and P exhibited reduced aqueous concentrations along with lower electrical conductivity. However, hardening also increased the aqueous concentrations of Na and K, which may have likely been due to Na- and K- sulphates/chlorides present as a result of hardening. Below pH 5, hardened ash showed little difference in leachate composition (of major inorganic elements leached) and electrical

conductivity, indicating similar dissolution of minerals as non-hardened bottom ash. Similar to the major inorganic elements leached, the trace metals As, Cd, Co, Hg, Ni, and Pb showed much lower leachability from hardened bottom ash compared to bottom ash.

The low aqueous concentrations of As, Cd, Co, Cu, and Zn at high pH, and increasing aqueous concentration as pH declined, was likely in part due to the adsorption of these trace metals to calcite forming at high pH. Additionally, the declining aqueous concentration of Cr, Hg, Mo, and Pb as pH declined was likely due to trace metal adsorption to Fe- and Al-oxides/hydroxides. At high pH, the aqueous concentration of very few trace metals exceed allowable limits set by BCCSR, but many of the allowable limits were exceeded as the acidity of the ash-water mixture fell below pH 5. In a landfill situation, monitoring leachate and the surrounding aqueous environment for pH decreases would be important as the aqueous concentrations of trace metals may start to exceed allowable limits.

4.0 CONCLUSION

Biomass ash may be used as a soil amendment to raise soil pH, and supply essential plant nutrients to agricultural crops or to forest tree species. However, there are concerns about the mobility of environmentally-sensitive constituents (i.e. trace elements) originating from ash. Few studies have investigated the long-term mobility of ash components. In addition, little is known about how ash constituents may interact with fine-textured soils, which are common in north-central British Columbia. Untreated ash is in some cases quite reactive, and the fine-texture of biomass ash makes it dusty and prone to air transport when handled or applied to land. Hardening is one way ash can be made less reactive and easier to handle. The overall goal of this study was to determine the suitability of UNBC gasifier bottom ash as a soil amendment, that is to simulate the long-term leachability of constituents contained within biomass bottom ash as influenced by a hardening process, and when this ash interacts with soil. The results of the study are also relevant to situations where biomass ash is landfilled or stockpiled, since leachates originating from ash would likely come in to contact with soil if they migrate downwards from a landfill or storage site. This work had two objectives. First, to determine the leachability of major and trace elements in both hardened and non-hardened bottom ash, with and without the presence of a fine-textured soil. Second, to determine the leachability of major and minor elements in both hardened and non-hardened bottom ash in response to acidification.

To address the first objective, the solid phases of bottom ash, hardened bottom ash, and the soil were analyzed by ICP-OES (following microwave acid digestion) to determine elemental content while pH was measured to determine alkalinity, and electrical conductivity (EC) was measured to determine salinity (Chapter 2). Five treatments (bottom ash, hardened bottom ash, soil control, and two ash-soil mixes) were then artificially weathered through 20-day serial batch extractions (Chapter 2). The extracts from the 20-day serial batch extractions were analyzed by

ICP-MS for elemental content, pH for alkalinity, EC for salinity, and anions were analyzed by ion-chromatography. The residual solid phase was also analyzed by ICP-OES to determine final elemental content. MINTEQ was used to predict saturated minerals that might be present within the aqueous phase of weathered ash treatments (Chapter 2). The second objective was addressed by the acidification of bottom ash and hardened bottom ash in single batch extractions. Elemental analysis of the collected extracts was then performed by ICP-MS (Chapter 3).

Bottom ash and hardened bottom ash were primarily composed of Ca, Fe, K, Al, Mg, Mn, P, Na, and S, with the remainder being composed of B, Ba, Sr, As, Co, Cr, Cu, Mo, Ni, and Zn. Weathering of bottom ash revealed that the leachate was dominated by Ca, K, Si, Al, Ba, Na, and SO_4^{-2}, which was also accompanied by a high electrical conductivity. Hardening primarily influenced the elemental leachability from bottom ash during the initial stages of weathering by reducing the aqueous electrical conductivity, and aqueous concentrations of Al, Ba, Ca, Cu, Hg, Sr, and Zn. However, due to hardening, B, Cr, K, Mo, Na, P, Sb, Se, Si, and SO_4^{-2} exhibited an increase in initial aqueous concentration. Trace metal leaching resulting from both ashes was minimal, and was likely due to the high pH and the adsorption of trace metals to secondary minerals. The high pH of bottom ash and hardened bottom ash make it ideal for use as a soil amendment to ameliorate acidic forest or agricultural soils.

Simulated long-term weathering of ash-soil mixtures revealed that when mixed with soil, bottom ash and hardened bottom ash leachability does not vary much. Largely, the leachate composition of ash-soil mixtures was not that different from the soil-only leachates. The long-term weathering experiment showed that solution concentrations of major inorganic elements in ash-soil mixtures were generally lower than those from ash-only treatments, but some of the minor elements (As, Cr, Hg, and Mo) exhibited higher solution concentrations in ash-soil mixtures compared to soil-only treatment, but did not exceed any allowable aquatic limits.

Compared to the high pH of ash-only mixtures, the neutral pH environment of the ash-soil mixtures in water likely attributed to the increased aqueous concentrations of As, Cr, Hg, and Mo. Generally, due to the sorptive properties of soil, many of the trace metals originating from ash were likely adsorbed to minerals present within soil. As a soil amendment, the elemental composition of bottom ash did not exceed sensitive trace metal content by SACoP, but did exceed the B limit for Alberta and the Ni limit for Denmark.

As the normal pH of ash-water mixtures is high, acidification of bottom ash and hardened bottom ash was found to alter the solubility of constituents contained in ash (Chapter 3). Such a situation may arise if ash were stored or added to highly acidic environments. Declining pH increased the aqueous concentrations of Ca, Mg, Mn, and Si, and minor elements As, B, Ba, Cd, Co, Cu, Ni, Sr, and Zn. Aqueous concentrations of Hg, Mo, Ni, and Pb were found to decrease as pH declined. The elements As and P were found to have increased aqueous concentrations at neutral pH. Hardening lowered leachability of the minor elements As, Cd, Co, Hg, Ni, and Pb, and major inorganic elements Ca, Fe, Mn, and P. Trace metals tend to have lowered mobility at higher pH, but as pH lowered many of the trace metals tend to increase in aqueous concentration and exceed allowable aquatic criteria. If landfilled, ash would have to be carefully monitored to make sure that the pH of the leachate does not drop much below pH 5.

Overall, there is potential for the use of UNBC gasifier bottom ash as a soil amendment. The high pH of both hardened and non-hardened bottom ash would make it a good liming agent. No solid phase limits were exceeded according to the SACoP. As a result of hardening, electrical conductivity and the release of constituents were lowered during simulated weathering. The mobility of trace metals was minimal, and the addition of ash to soil showed little influence on the resulting leachate chemistry as compared to extracts obtained from soil-only.

Further investigation into different application rates of ash to soil are important, as higher concentrations of ash may overload the buffering capacity of soil, and leachability of ash-soil mixes are likely to alter (especially those of trace elements of concern). Investigation of ash to soil mixes would inevitably lead to field studies involving ash applications in soil regarding forestry or agriculture. Additionally, the lab-hardening technique of biomass ash (wetting) should be further studied to determine whether a more suitable hardening process might yield better granules (e.g. the introduction of more/and steady application of carbon dioxide to help the hardening process, or the continual wetting of the ash material throughout the hardening process).

LITERATURE CITED

Adriano, D.C.; **2001**. Trace Elements in Terrestial Environments. 2nd Edition. Springer-Verlag, New York, New York.

Alberta Environment. Standards and Guidelines for the Use of Wood Ash as a Liming Material for Agricultural Soils. **July 2002**. Pub. No: T/666. 1-8.

Arvidsson, H.; Lundkvist, H.; Effects of crushed wood ash on soil chemistry in young Norway spruce stands. *Forest Ecology and Management.* **2003.** *176,* 121-132.

Arvidsson, H.; Vestin, T.; Lundkvist, H.; Effects of crushed wood ash application on ground vegetation in young Norway spruce stands. *Forest Ecology and Management.* **2002.** *161,* 75-87.

Augusto, L.; Bakker, M.R.; Meredieu, C.; Wood ash applications to temperate forest ecosystems – potential benefits and drawbacks. *Plant Soil.* **2008.** *306,* 181-198.

Bohn, H.L.; McNeal, B.L.; O'Conner, G.A.; **1985.** Soil Chemistry. 2nd Edition, John Wiley and Sons, New York, New York.

Brady, N.C.; Weil, R.R. **2002.** The Nature and Properties of Soils, 13th Edition. Pearson Education, Inc.. Stephen Helba. Upper Saddle River, New Jersey. Pp 6.

Canadian Certified Reference Materials Project (CCRMP).; Certificate of Analysis TILL-1, TILL-2, TILL-3, and TILL-4, Geochemical Soil and Till Reference Materials. *Geostandards Newsletter.* **1995.** wbowman@emr1.emr.ca.

Chapman, H.D.; **1965.** Cation-exchange capacity. *In:* C.A. Black (ed.). Methods of soil analysis – Chemical and microbiological properties. Agronomy 9: 891-901.

Chimenos, J.M.; Fernandez, A.I.; Nadal, R.; Espiell, F.; Short-term natural weathering of MSWI bottom ash. *Journal of Hazardous Materials.* **2000.** *B79,* 287-299.

Clark, M.J.R. (editor). **2003.** British Columbia Field Sampling Manual. Water, Air and Climate Change Branch, Ministry of Water, Land and Air Protection, Victoria, BC, Canada.

Comans, R.B.J.; Middelburg, J.J.; Sorption of trace metals on calcite: Applicability of the surface precipitation model. *Geochmica et Cosmochimica Acta.* **1987.** *51,* 2587-2591.

Demeyer, A.; Nkana, J.C.V.; Verloo, M.G.; Characteristics of wood ash and influence on soil properties and nutrient uptake: an overview. *Bioresource Technology.* **2001.** *77,* 287-295.

Dijkstra, J.J.; van der Sloot, H.A.; Comans, R.N.J.; The leaching of major and trace elements from MSWI bottom ash as a function of pH and time. *Applied Geochemistry.* **2006.** *21,* 335-351.

Dudas, M.J.; Long-Term Leachability of Selected Elements from Fly Ash. *Environmental Science & Technology.* **1981.** *15,* 840-843.

Environmental Management Act. Province of British Columbia Regulation of the Minister of Environment and Minister Responsible for Water Stewardship and Sustainable Communities. **June 2007.** R 370/2007/14, 1-11. (Access Date: July 12, 2012, http://www.env.gov.bc.ca/epd/industrial/regs/codes/soil_amend/pdf/soil_amend_1849_001.pdf)

EPRI. Use of Batch and Column Methodologies to Assess Utility Waste Leaching and Subsurface Chemical Attenuation. **May 1991.** EPRI EN-7313. Prepared by Battelle, Pacific Northwest Laboratories (Richland, Washington).

Eriksson, H.; Short-term effects of granulated wood ash on forest soil chemistry in SW and NE Sweden. *Scandinavian Journal of Forestry Research Suppl.*. **1998.** *2,* 43-55.

Fallman, A.-M., Aurell, B.; Leaching tests for environmental assessment of inorganic substances in wastes, Sweden. *The Science of the Total Environment.* **1996.** *178,* 71-84.

Fransman, B.; Nihlgard, B.; Water chemistry in forested catchments after topsoil treatments with liming agents in south Sweden. *Water Air Soil Pollut.*. **1995.** *85,* 895-900.

Goh, T.B.; Mermut, A.R.; Chapter 20 in Carter, M.R. and E.G. Gregorich. **2008**. Soil Sampling and Methods of Analysis. 2nd Edition. CRC Press, Taylor and Francis Group, Boca Raton, FL. Pages 215-223.

Gori, M.; Bergfeldt, B.; Pfrang-Stotz, G.; Reichelt, J.; Sirini, P.; Effect of short-term natural weathering on MSWI and wood waste bottom ash leaching behaviour. *Journal of Hazardous Materials.* **2011.** *189,* 435-443.

Haglund, N.; Guideline for Classification of Ash from Solid Biofuels and Peat Utilised for Recycling and Fertilizing in Forestry and Agriculture. *Noridc Innovation Centre. ISSN 0283-7234. Norway,* **2008.** 1-34.

Hanell, B.; Magnusson. T.; An evaluation of land suitability for forest fertilization with biofuel ash on organic soils in Sweden. *Forest Ecology and Management.* **2005.** *209,* 43-55.

Holmberg, S.L.; Lind, B.B.; Claesson, T.; Chemical composition and leaching characteristics of granules made of wood ash and dolomite. *Environmental Geology.* **2000.** *40 (1/2),* 1-10.

Isayama, Y.; Saka, S.; Biodisel production by supercritical process with crude bio-methanol prepared by wood gasification. *Bioresource Technology.* **2008.** *99,* 4775-4779.

Jacobson, S.; Hogbom, L.; Ring, E.; Nohrstedt, H.; Effects of wood ash does and formulation on soil chemistry at two coniferous forest sites. *Water, Air, and Soil Pollution.* **2004.** *158,* 113-125.

Jacobson, S.; Gustafsson, L.; Effects on ground vegetation of the application of wood ash to a Swedish Scots pine stand. *Basic and Applied Ecology.* **2001.** *2,* 233-241.

Johnson, C.A.; Brandenberger, S.; Baccini, P.; Acid neutralizing capacity of municipal waste incinerator bottom ash. *Environmental Science & Technology.* **1995**. *29,* 142-147.

Johnsson, L.; Effect of acidification on retention, leaching and loss of selenium in a podzol profile – a laboratory study. *Ecological Bulletins.* **1995.** *44,* 123-128.

Kahl, J.; Fernandez, I.; Rustad, L.; Peckenham, J.; Threshold application rates of wood ash to an acidic forest soil. *Journal of Environmental Quality.* **1996.** *25,* 220-227.

Kalra, Y.P.; Maynard, D.G.; **1991.** Methods Manual for Forest Soil and Plant Analysis. Information Report NOR-X-319. Forestry Canada, Northwest Region, Northern Forestry Centre, Edmonton, Alberta, Canada.

Kirby C.S.; Rimstidt, J.D.; Mineralogy and Surface Properites of Municipial Solid Waste Waste Ash. *Environmental Science & Technology.* **1993.** *27,* 652-660.

Krejsl, J.A.; Scanlon, T.M.; Evaluation of beneficial use of wood-fired boiler ash on oat and bean growth. *Journal of Environmental Quality.* **1996.** *25,* 950-954.

Leco Corporation, 2008; Leco Truspec Add-On Module, Instruction Manual, Software Version 1.9x, Part Number 200-705. **July 2008**.

Leiva, C.; Vilches, L.F.; Vale, J.; Fernandez-Pereira, C.; Fire resistance of biomass ash panels used for internal partitions in buildings. *Fire Safety Journal.* **2009.** *44,* 622-628.

Leiva, C.; Vilches, L.F.; Vale, J.; Fernandez-Pereria, C.; Influence of the type of ash on the fire resistance characteristics of ash-enriched mortars. *Fuel.* **2005.** *84,* 1433-1439.

Lewin, K.; Leaching tests for waste compliance and characterisation: recent practical experiences. *The Science of the Total Environment.* **1996.** *178,* 85-94.

Liao, C.; Wu, C.; Yan, Y.; The characteristics of inorganic elements in ashes from a 1MW CFB biomass gasification power generation plant. *Fuel Processing Technology.* **2007.** *88,* 149-156.

Ma, J.F.; Chapter 7 – Functions of silicon in plant growth. *Soil, Fertilizer, and Plant Silicon Research in Japan.* **2002.** 107-180. http://dx.doi.org/10.1016/B978-044451166-9/50007-5

Mahmood, S.; Finlay, R.D.; Wallander, H.; Erland, S.; Ectomycorrhizal colonisation of roots and ash granules in a spruce forest treated with granulated wood ash. *Forest Ecology and Management.* **2002.** *160,* 65-74.

McBride, M.B.; **1994.** Environmental Chemistry of Soils. Oxford University Press. New York, New York. Page 406.

McKendry, P.; Energy production from biomass (part 1): overview of biomass. *Bioresource Technology.* **2002a.** *83,* 37-46.

McKendry, P.; Energy production from biomass (part 3): gasification technologies. *Bioresource Technology.* **2002b.** *83,* 55-63.

Meima, J.A.; Comans, R.N.J.; Application of Surface Complexation/Precipitation Modeling to Contaminant Leaching from Weathered Municipal Solid Waste Incinerator Bottom Ash. *Environmental Science and Technology.* **1998.** *32,* 688-693.

Meima, J.A.; Comans, R.N.J.; Geochemical Modeling of Weathering Reactions in Municipal Solid Waste Incinerator Bottom Ash. *Environmental Science and Technology.* **1997.** *31,* 1269-1276.

Meima, J.A.; Comans, R.N.J.; The leaching of trace elements from municipal solid waste incinerator bottom ash at different stages of weathering. *Applied Geochemistry.* **1999.** *14,* 159-171.

Meyers, N.; Kopecky, M.J.; Industrial wood ash as a soil amendment for crop production. *Tappi Journal.* **1998.** *81(4),* 123-130.

Middleburg, J.J.; Comans, R.N.J.; Sorption of cadmium on hydroxyapatite. *Chemical Geology.* **1991.** *90,* 45-53.

Moilanen, M.; Fritze, H.; Nieminen, M.; Piirainen, S.; Issakainen, J.; Piispanen, J.; Does wood ash application increase heavy metal accumulation in forest berries and mushrooms? *Forest Ecology and Management.* **2006.** *226,* 153-160.

Muse, J.K.; Mitchell, J.K.; Paper mill boiler ash and lime by-products as soil liming materials. *Agronomy Journal.* **1995.** *87(3),* 432-438.

Naylor, L.M.; Schmidt, E.J.; Agricultural use of wood ash as a fertilizer and liming material. *Tappi Journal.* **1986.** *69(10),* 114-119.

Neupane, G.; Donahoe, R.J.; Leachability of elements in alkaline and acidic coal fly ash samples during batch and column leaching tests. *Fuel.* **2012.** http://dx.doi.org/10.1016/j.fuel.2012.06.013

Nkana, J.C.V.; Demeyer, A.; Verloo, M.G.; Chemical effects of wood ash on plant growth in tropical acid soils. *Bioresource Technology.* **1998.** *63,* 251-260.

Ozolincius, R.; Buozyte, R.; Varnagiryte-Kabasinskiene, I.; Wood ash and nitrogen influence on ground vegetation cover and chemical composition. *Biomass and Bioenergy.* **2007b.** *31,* 710-716.

Ozolincius, R.; Varnagiryte-Kabasinskiene, I.; Stakenas, V.; Miksys, V.; Effects of wood ash and nitrogen fertilization on Scots pine crown biomass. *Biomass and Bioenergy.* **2007a.** *31,* 700-709.

Park, B.B.; Yanai, R.D.; Sahm, J.M.; Lee, D.K.; Abrahamson, L.P.; Wood ash effects on plant and soil in a willow bioenergy plantation. *Biomass and Bioenergy.* **2005.** *28,* 355-365.

Patterson, S.J.; Acharya, S.N.; Thomas, J.E.;. Barley biomass and grain yield and canola seed response to land application of wood ash. Agron. J.. **2004**. *96*, 971-977.

Penniall, C.L.; Williamson, C.J.; Feasibility study into the potential for gasification plant in the New Zealand wood processing industry. *Energy Policy.* **2009.** *37,* 3377-3386.

Pichtel, J.; **2005.** Waste Management Practices, Municipal, Hazardous and Industrial. CRC Press, Taylor and Francis Group. Boca Raton, FL. pp. 261-272.

Piiraninen, S.; Ash fertilisation and leaching of nutrients from drained peatland. *SkogForsk Report.* **2001.** *No. 2,* pp. 21-24.

Pitman, R.M.; Wood ash use in forestry – a review of the environmental impacts. *Forestry.* **2006.** *79(5),* 563-588.

Quina, M.J.; Bordado, J.C.M.; Quinta-Ferreira, R.M.; The influence of pH on the leaching behaviour of inorganic components from municipal solid waste APC residues. *Waste Management.* **2009.** *29,* 2483-2493.

Rajamma, R.; Ball, R.J.; Tarelho, L.A.C.; Allen, G.C.; Labrincha, J.A.; Ferreira, V.M.; Characterisation and use of biomass fly ash in cement-based materials. *Journal of Hazardous Materials.* **2009.** *172,* 1049-1060.

Rehl, E.; Reimer, K.B.; Rutherford, P.M.; A short term study on the mobility of select metals from loose and hardened UNBC pellet plant bottom and fly ash by sequential batch extraction. **2010.** *(Unpublished student project).*

Ring, E.; Jacobson, S.; Nohrstedt, H.; Soil-solution chemistry in a coniferous stand after adding wood ash and nitrogen. *Canadian Journal of Forest Research.* **2006.** 36, 153-163.

Saarsalmi, A.; Derome, J.; Levula, T.; Effect of wood ash fertilisation on stand growth, soil, water and needle chemistry, and berry yield of lignoberry (Vaccinium vitis-idaea L.) in a Scots pine stand in Finland. *Metsandulskid For. Stud..* **2005.** *42,* 13-33.

Sarenbo, S.; Wood ash dilemma-reduced quality due to poor combustion performance. *Biomass and Bioenergy.* **2009.** *33,* 1212-1220.

Shannon, D.G.; Fine, L. O.; Cation Solubilities of Lignite Fly Ashes. *Environmental Science & Technology.* **1974.** *8(12),* 1026-1028.

Skjemstad, J.O.; Baldock, J.A.; Total and organic carbon. Chapter 21 in Carter, M.R. and E.G. Gregorich, Soil Sampling and Methods of Analysis, 2nd Edition. CRC Press, Taylor and Francis Group, Boca Raton, FL. **2008.** Pages 225-237.

Steenari, B-M.; Karlsson, L.G.; Lindqvist, O.; Evaluation of the leaching characteristics of wood ash and the influence of ash agglomeration. *Biomass and Bioenergy.* **1999.** *16,* 119-136.

Steenari, B-M.; Lindqvist, O.; Stabilisation of biofuel ashes for recycling to forest soil. *Biomass and Bioenergy.* **1997.** *13(1/2),* 39-50.

SYLVIS Environmental. Land Application Guidelines for the Organic Matter Recycling Regulation and the Soil Amendment Code of Practice – Best Management Practices. March 2008. Document #758-08. 1-300.

Talbot, R.W.; Anderson, M.A.; Andren, A.W.; Qualitative Model of Heterogeneous Equilibira in a Fly Ash Pond. *Environmental Science & Technology.* **1978.** *12(9),* 1056-1062.

Theis, T.L.; Wirth, J.L.; Soprtive Behavior of Trace Metals on Fly Ash in Aqueous Systems. *Environmental Science & Technology.* **1977.** *11(12),* 1096-1100.

USEPA Method 1311. Toxicity Characteristic leaching Procedure. Revision 0. July 1992. 1311-1 to 1311-35.

USEPA Method 200.8. Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma – Mass Spectrometry. Revision 5.4. 1994. 200.8-1 to 200.8-51.

USEPA Method 3050B. Acid Digestion of Sediments, Sludges, and Soils. Revision 2. December 1996. 3050B-1 to 3050B-12.

USEPA Method 8221. Alkalinity – USEPA Buret Titration Method. DOC316.53.01151. Hach Company. February 2008, Edition 5.

Van der Sloot, H.A.; Comans, R.N.J.; Hjelmar, O.; Similarities in the leaching behaviour of trace contaminants from waste, stabilized waste, construction materials and soils. *The Science of the Total Environment.* **1996.** *178,* 111-126.

Venner, K.H.; Preston, C.M.; Prescott, C.E.; Characteristics of wood wastes in British Columbia and their potential suitability as soil amendments and seedling growth media. *Canadian Journal of Soil Science.* **2011.** *91,* 95-106.

Vitkova, M.; Ettler, V.; Sebek, O.; Mihaljevic, M.; Grygar, T.; Rohovec, J.; The pH-dependent leaching of inorganic contaminants from secondary lead smelter fly ash. *Journal of Hazardous Materials.* **2009.** *167,* 427-443.

Wahlstrom, M.; Nordic recommendation for leaching tests for granular waste materials. *The Science of the Total Environment.* **1996.** *178,* 95-102.

Wang, S.; Miller, A.; Llamazos, E.; Fonseca, F.; Baxter, L.; Biomass fly ash in concrete: Mixture proportioning and mechanical properties. *Fuel.* **2008.** *87,* 365-371.

Warren, C.J.; Dudas, M.J.; Formation of Secondary Minerals in Artificially Weathered Fly Ash. *Journal of Environmental Quality.* **1985.** *14(3),* 405-409.

Williams, T.; Hollis, C.; Smith, B.; Forest soil and water chemistry following bark boiler bottom ash applications. *Journal of Environmental Quality.* **1996.** *25,* 955-961.

Williams, T.M.; Obtaining water quality permits for land application of biomass boiler ash. *Biomass and Bioenergy.* **1997.** *13,* 279-287.

Wolery, T.J.; EQ3NR, A Computer Program for Geochemical Aqueous Speciation-Solubility Calculations. Users Guide and Documentation, UCRL-53414. Lawrence Livermore National Laboratory, Livermore, California, 1983.

Yan, J.; Baverman, C.; Moreno, L.; Neretnieks, I.; Evaluation of the time-dependent neutralising behaviours of MSWI bottom ash and steel slag. *The Science of the Total Environment.* **1998**. *216*, 41-54.

Yusiharni, E.; Gilkes, R.; Minerals in the ash of Australian native plants. *Geoderma.* **2012,** *189/190,* 369-380.

Zevenbergen, C.; Van Reeuwijk, L.P.; Bradley, J.P.; Comans, R.N.J.; Shuiling, R.D.; Weathering of MSWI bottom ash with emphasis on the glassy constituents. *Journal of Geochemical Exploration.* **1998.** *62,* 293-298.

APPENDICES TABLE OF CONTENTS

APPENDIX A1
Solid Phase and Aqueous Phase Data

Table A1.0 - Selected properties of non-weathered solid phase BA/FA mix, FA, TILL3 (reference material) and leftover HBA from sieving (HBA powder), where elemental content (except for C, N and S via dry combustion) was measured by ICP-OES following concentrated HCl/HNO_3 digestion; n=4.

Parameter	BA/FA Mix		FA		TILL 3		HBA Powder	
	Mean	*SD*	*Mean*	*SD*	*Mean*	*SD*	*Mean*	*SD*
Moisture Content (%)	0.152	0.015	1.37	0.08	0.995	0.019	0.726	0.033
Total N (%)	0.0190	0.0008	0.170	0.005	n/a	n/a	0.0159	0.0013
Total S (%)	n/a	n/a	2.13	0.07	n/a	n/a	n/a	n/a
Total C (inorganic)	1.43	0.07	4.50	0.52	0.0836	0.0171	1.75	0.09
Total C (organic)	2.60	0.13	9.67	0.655	0.940	0.091	1.81	0.18
Total C (%)	4.03	0.11	14.2	0.4	1.02	0.09	3.56	0.16
CCE (%)	29.4	0.8	n/a	n/a	n/a	n/a	30.1	1.0
Elemental Content via ICP-OES following HCl/HNO_3 digestion								
Ag (ppm)	<1.0	n/a	<1.0	n/a	<1.0	n/a	<1.0	n/a
Al (%)	1.84	0.06	1.14	0.04	1.40	0.06	1.74	0.02
As (ppm)	7.04	1.04	4.65	0.94	86.9	1.0	7.35	0.42
B (ppm)	149	2	366	7	8.07	0.93	144	7
Ba (ppm)	1233	18	2053	15	57.7	3.3	1391	31
Be (ppm)	<1.0	n/a	<1.0	n/a	<1.0	n/a	<1.0	n/a
Bi (ppm)	<1.0	n/a	<1.0	n/a	<1.0	n/a	<1.0	n/a
Ca (%)	11.7	0.5	24.8	0.6	0.725	0.028	11.2	0.4
Cd (ppm)	6.18	0.29	119	3	<1.0	n/a	<1.0	n/a
Co (ppm)	14.0	0.2	7.78	0.36	30.9	5.8	15.0	0.5
Cr (ppm)	36.2	1.2	30.2	2.0	75.5	2.1	40.8	1.6
Cu (ppm)	52.5	1.3	140	4	19.0	0.9	49.3	1.7

Table A1.0 - Selected properties of non-weathered solid phase BA/FA mix, FA, TILL3 (reference material) and leftover HBA from sieving (HBA powder), where elemental content (except for C, N and S via dry combustion) was measured by ICP-OES following concentrated HCl/HNO_3 digestion (continued).

Parameter	BA/FA Mix		FA		TILL 3		HBA Powder	
	Mean	*SD*	*Mean*	*SD*	*Mean*	*SD*	*Mean*	*SD*
Fe (%)	1.62	0.08	0.973	0.050	2.06	0.05	1.56	0.03
Hg (ppm)	<2.0	n/a	<2.0	n/a	<2.0	n/a	<2.0	n/a
K (%)	2.26	0.02	5.77	0.12	0.192	0.010	2.08	0.09
Li (ppm)	18.4	0.8	231	6	28.4	0.7	12.0	0.3
Mg (%)	1.48	0.06	3.10	0.07	0.644	0.011	1.34	0.04
Mn (%)	0.739	0.029	1.63	0.04	0.034	0.001	0.660	0.024
Mo (ppm)	6.01	0.09	12.5	0.1	<1.0	n/a	6.17	0.18
Na (%)	0.464	0.009	0.263	0.006	0.048	0.002	0.447	0.017
Ni (ppm)	54.8	2.3	91.2	13.8	33.6	0.6	63.0	2.6
P (%)	0.560	0.016	1.32	0.03	0.051	0.002	0.591	0.027
Pb (ppm)	2.26	0.18	43.2	0.5	13.0	0.4	<2.0	n/a
S (%)	0.113	0.013	0.104	0.007	0.015	0.001	0.132	0.006
Sb (ppm)	<4.0	n/a	<4.0	n/a	<4.0	n/a	<4.0	n/a
Sn (ppm)	7.36	0.10	54.5	2.9	<1.0	n/a	2.45	0.51
Sr (ppm)	412	6	706	13	46.1	3.7	446	8
Ti (ppm)	947	70	321	22	1344	43	1019	67
Tl (ppm)	<2.0	n/a	<2.0	n/a	<2.0	n/a	<2.0	n/a
U (ppm)	<20	n/a	<20	n/a	<20	n/a	<20	n/a
V (ppm)	42.6	0.7	15.0	0.4	53.3	1.5	46.8	1.3
Y (ppm)	<2.0	n/a	<2.0	n/a	<2.0	n/a	<2.0	n/a
Zn (ppm)	769	26	5505	122	51.3	2.2	115	8
Zr (ppm)	16.4	1.5	9.24	2.30	15.4	1.1	14.9	0.5

**A sample of bottom and fly ash mix was collected from the active collection bin and a separate sample of pure fly ash on June 27, 2011*

Table A1.1 – Selected properties of weathered solid-phase bottom ash, hardened bottom ash, soil, 5%BA and 5%HBA, where elemental content (except for C, N and S via dry combustion) was measured by ICP-OES following concentrated HCl/HNO_3 digestion; n=4.

Parameter	**BA (Batch Extraction)**		**HBA (Batch Extraction)**		**Soil (Batch Extraction)**		**5%BA (Batch Extraction)**		**5%HBA (Batch Extraction)**	
	Mean	*SD*	*Mean*	*SD*	*Mean*	*SD*	*Mean*	*SD*	*Mean*	*SD*
Total N (%)	0.0131	0.000004	0.0124	0.0032	0.132	0.002	0.112	0.002	0.116	0.001
Total S (%)	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Total C (inorganic)	1.16	0.08	1.40	0.03	n/a	n/a	n/a	n/a	n/a	n/a
Total C (organic)	1.92	0.18	1.73	0.17	n/a	n/a	n/a	n/a	n/a	n/a
Total C (%)	3.07	0.16	3.13	0.17	2.13	0.03	1.97	0.07	2.04	0.04
Elemental Content via ICP-OES following HCl/HNO_3 digestion										
Ag (ppm)	<1.0	n/a	<1.0	n/a	<1.0	n/a	<1.0	n/a	<1.0	n/a
Al (%)	1.81	0.04	1.63	0.04	2.39	0.44	3.16	0.17	3.15	0.55
As (ppm)	5.78	1.94	6.21	1.42	6.29	0.48	7.03	0.93	6.88	0.56
B (ppm)	63.1	1.9	52.7	1.8	3.03	2.59	8.81	0.64	6.46	1.05
Ba (ppm)	1352	34	1169	10	252.8	32.5	393	12	345	12
Be (ppm)	<1.0	n/a	<1.0	n/a	<1.0	n/a	<1.0	n/a	<1.0	n/a
Bi (ppm)	<1.0	n/a	<1.0	n/a	<1.0	n/a	<1.0	n/a	<1.0	n/a
Ca (%)	8.44	0.07	8.55	0.10	0.542	0.022	0.942	0.010	0.960	0.121
Cd (ppm)	<1.0	n/a	<1.0	n/a	<1.0	n/a	1.20	n/a	<1.0	n/a
Co (ppm)	25.6	3.5	20.9	0.4	22.8	0.7	23.6	0.1	23.1	0.6
Cr (ppm)	35.0	1.7	31.1	1.7	43.8	4.1	53.1	2.1	49.2	1.8
Cu (ppm)	59.7	6.5	50.0	4.7	18.4	0.6	20.4	0.3	20.0	0.2
Fe (%)	1.79	0.15	1.64	0.09	2.96	0.07	3.09	0.08	3.37	0.58
Hg (ppm)	<2.0	n/a	<2.0	n/a	<2.0	n/a	<2.0	n/a	<2.0	n/a
K (%)	1.66	0.01	1.40	0.04	0.345	0.112	0.610	0.053	0.501	0.055
Li (ppm)	12.9	0.6	11.1	0.6	23.7	2.4	29.7	1.6	27.5	1.1

Table A1.1 – Selected properties of weathered solid-phase bottom ash, hardened bottom ash, soil, 5%BA and 5%HBA, where elemental content (except for C, N and S via dry combustion) was measured by ICP-OES following concentrated HCl/HNO_3 digestion (continued).

Parameter	BA (Batch Extraction)		HBA (Batch Extraction)		Soil (Batch Extraction)		5%BA (Batch Extraction)		5%HBA (Batch Extraction)	
	Mean	*SD*	*Mean*	*SD*	*Mean*	*SD*	*Mean*	*SD*	*Mean*	*SD*
Mg (%)	1.45	0.01	1.25	0.02	0.698	0.009	0.782	0.023	0.826	0.125
Mn (%)	0.714	0.004	0.581	0.008	0.111	0.006	0.142	0.002	0.149	0.025
Mo (ppm)	2.98	0.27	2.72	0.19	<1.0	n/a	<1.0	n/a	<1.0	n/a
Na (%)	0.442	0.015	0.374	0.006	0.042	0.009	0.081	0.006	0.066	0.008
Ni (ppm)	98.8	51.8	55.5	1.0	28.5	0.8	31.7	0.7	30.9	0.7
P (%)	0.509	0.011	0.441	0.012	0.105	0.002	0.128	0.001	0.127	0.002
Pb (ppm)	<2.0	n/a	<2.0	n/a	4.62	0.80	3.68	0.38	3.79	0.23
S (%)	0.034	0.002	0.031	0.001	0.011	0.001	0.010	0.001	0.011	0.0003
Sb (ppm)	<4.0	n/a	<4.0	n/a	<4.0	n/a	<4.0	n/a	<4.0	n/a
Sn (ppm)	2.46	0.86	0.880	0.277	<1.0	n/a	<1.0	n/a	<1.0	n/a
Sr (ppm)	383	2	355	4	61.3	7.6	92.0	1.4	82.1	2.3
Ti (ppm)	1003	28	943	30	1419	150	1501	131	1603	44
Tl (ppm)	<2.0	n/a	<2.0	n/a	<2.0	n/a	<2.0	n/a	<2.0	n/a
U (ppm)	<20	n/a	<20	n/a	<20	n/a	<20	n/a	<20	n/a
V (ppm)	47.1	3.2	44.3	2.1	92.3	8.2	107	3	101	3
Y (ppm)	<2.0	n/a	<2.0	n/a	<2.0	n/a	<2.0	n/a	<2.0	n/a
Zn (ppm)	100	17	79.1	2.5	126	1	141	3	141	2
Zr (ppm)	15.9	0.9	16.1	1.2	8.70	5.75	18.6	0.9	12.5	4.0

Table A1.2 – Selected properties of non-weathered solid phase bottom ash, hardened bottom ash, fly ash, soil control, leftover HBA from sieving (HBA powder), BA/FA mix and TILL 3 (reference material), determined by ICP-OES following concentrated $HNO_3/HF/H_2BO_3$ digestion; n=4.

Parameter	BA		HBA		FA		Soil Control		HBA Powder		BA/FA Mix		TILL 3	
	Mean	*SD*	*Mean*	*SD*	*Mean*	*SD*	*Mean*	*SD*	*Mean*	*SD*	*Mean*	*SD*	*Mean*	*SD*
Elemental Content														
Ag (ppm)	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0
Al (%)	4.66	0.13	4.88	0.11	1.35	0.02	7.29	0.16	4.50	0.03	4.56	0.10	6.65	0.11
As (ppm)	<12	<12	<12	<12	<12	<12	<12	<12	<12	<12	<12	<12	<12	<12
Ba (ppm)	1949	29	1789	54	2500	128	756	13	1964	34	1701	51	447	4
Be (ppm)	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0
Bi (ppm)	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0
Ca (%)	13.8	0.3	12.3	0.4	29.9	0.2	0.966	0.023	13.9	0.6	14.2	0.5	1.92	0.03
Cd (ppm)	<3.0	<3.0	<3.0	<3.0	103	1	<3.0	<3.0	<3.0	<3.0	6.13	0.22	<3.0	<3.0
Co (ppm)	22.2	1.6	20.1	1.2	8.12	0.50	27.5	1.5	18.6	0.4	17.0	0.5	32.5	5.2
Cr (ppm)	63.8	7.5	62.1	10.9	36.0	2.0	63.5	3.3	67.5	5.5	54.2	3.7	97.8	3.9
Cu (ppm)	66.2	0.8	64.7	4.0	152	4	22.1	0.4	66.5	2.0	71.1	2.1	22.2	0.6
Fe (%)	2.51	0.08	2.66	0.14	1.25	0.05	3.71	0.08	2.50	0.04	2.51	0.06	2.90	0.02
Hg (ppm)	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0
K (%)	3.65	0.10	3.54	0.04	5.32	0.09	1.62	0.04	3.49	0.04	3.68	0.09	2.18	0.03
Li (ppm)	13.0	0.3	13.0	0.5	121	1	25.4	0.4	12.6	0.2	16.3	0.3	24.5	0.7
Mg (%)	1.83	0.03	1.74	0.06	3.63	0.03	0.975	0.024	1.84	0.04	1.95	0.05	1.09	0.02
Mn (%)	0.770	0.017	0.683	0.027	1.79	0.02	0.124	0.006	0.787	0.032	0.848	0.023	0.0518	0.0008
Mo (ppm)	5.35	1.25	6.24	0.35	12.8	0.2	<3.0	<3.0	6.49	0.45	6.07	0.21	<3.0	<3.0
Na (%)	1.42	0.06	1.54	0.04	0.299	0.008	1.70	0.04	1.37	0.02	1.42	0.03	2.03	0.03
Ni (ppm)	72.9	11.0	71.0	6.6	95.3	6.2	31.8	0.4	74.4	4.4	62.9	1.9	40.1	0.3
P (%)	0.568	0.023	0.505	0.017	1.16	0.01	0.124	0.002	0.570	0.024	0.525	0.015	0.0529	0.0004
Pb (ppm)	<6.0	<6.0	<6.0	<6.0	41.7	0.4	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	16.9	1.2
S (%)	0.166	0.029	0.171	0.010	2.74	0.01	0.0105	0.0084	0.240	0.011	0.385	0.018	0.00306	0.00427
Sb (ppm)	<12	<12	<12	<12	<12	<12	<12	<12	<12	<12	<12	<12	<12	<12

Table A1.2 – Selected properties of non-weathered solid phase bottom ash, hardened bottom ash, fly ash, soil control, leftover HBA from sieving (HBA powder), BA/FA mix and TILL 3 (reference material), determined by ICP-OES following concentrated $HNO_3/HF/H_2BO_3$ digestion (continued).

Parameter	BA		HBA		FA		Soil Control		HBA Powder		BA/FA Mix		TILL 3	
	Mean	*SD*	*Mean*	*SD*	*Mean*	*SD*	*Mean*	*SD*	*Mean*	*SD*	*Mean*	*SD*	*Mean*	*SD*
Sn (ppm)	9.00	0.04	7.80	0.82	69.7	1.1	<3.0	<3.0	10.3	0.9	16.0	0.4	<3.0	<3.0
Sr (ppm)	519	8	479	14	639	12	208	5	515	16	457	16	273	3
Ti (ppm)	2215	55	2301	69	385	26	5250	143	2203	17	2089	64	2690	39
Tl (ppm)	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0
U (ppm)	<60	<60	<60	<60	<60	<60	<60	<60	<60	<60	<60	<60	<60	<60
V (ppm)	64.6	1.6	68.7	1.6	17.2	0.3	115	2	65.6	1.0	61.6	1.4	67.3	1.0
W (ppm)	142	22	110	7	63.7	3.2	17.0	2.5	109	12	92.0	5.0	167	58
Y (ppm)	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0
Zn (ppm)	117	15	102	11	5386	35	134	2	109	6	554	19	53	1
Zr (ppm)	56.1	3.1	56.1	2.9	19.2	5.5	98.1	12.1	54.7	2.5	54.1	2.3	129	14

Table A1.3 - Selected properties of weathered solid phase bottom ash, hardened bottom ash, soil, 5%BA and 5%HBA, determined by ICP-OES following concentrated $HNO_3/HF/H_2BO_3$ digestion; n=4.

Parameter	BA (Batch Extraction)		HBA (Batch Extraction)		Soil (Batch Extraction)		5%BA (Batch Extraction)		5%HBA (Batch Extraction)	
	Mean	*SD*	*Mean*	*SD*	*Mean*	*SD*	*Mean*	*SD*	*Mean*	*SD*
Elemental Content										
Ag (ppm)	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0
Al (%)	4.76	0.12	4.68	0.10	7.43	0.03	7.31	0.07	7.10	0.11
As (ppm)	<12	<12	<12	<12	<12	<12	<12	<12	<12	<12
Ba (ppm)	1830	75	1582	57	761	10	827	22	806	19
Be (ppm)	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0
Bi (ppm)	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0
Ca (%)	9.89	0.24	10.2	0.4	1.01	0.04	1.40	0.04	1.30	0.03
Cd (ppm)	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0
Co (ppm)	26.8	2.6	23.6	1.0	28.0	0.5	27.9	0.4	26.8	0.7
Cr (ppm)	57.7	5.5	53.1	6.8	63.1	2.4	63.8	0.2	60.4	0.5
Cu (ppm)	73.2	7.8	63.2	6.5	22.6	0.3	24.0	0.2	23.6	0.4
Fe (%)	2.67	0.17	2.59	0.17	3.75	0.02	3.69	0.04	3.57	0.04
Hg (ppm)	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0
K (%)	3.46	0.09	3.21	0.10	1.67	0.03	1.74	0.02	1.69	0.05
Li (ppm)	13.2	0.5	13.6	1.8	25.5	0.3	24.7	0.1	24.4	0.3
Mg (%)	1.87	0.04	1.70	0.08	1.00	0.01	1.01	0.02	0.968	0.012
Mn (%)	0.778	0.018	0.660	0.024	0.129	0.004	0.159	0.005	0.146	0.002
Mo (ppm)	3.12	<3.0	3.06	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0
Na (%)	1.39	0.03	1.39	0.03	1.73	0.02	1.72	0.03	1.67	0.04
Ni (ppm)	86.8	26.7	61.2	3.0	31.7	0.2	33.4	0.6	31.9	0.6
P (%)	0.587	0.020	0.510	0.017	0.123	0.001	0.138	0.003	0.133	0.001
Pb (ppm)	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0
S (%)	0.0608	0.0061	0.0428	0.0068	0.0152	0.0045	0.0152	0.0058	0.0105	0.0015

Table A1.3 - Selected properties of weathered solid phase bottom ash, hardened bottom ash, soil, 5%BA and 5%HBA, determined by ICP-OES following concentrated $HNO_3/HF/H_2BO_3$ (continued).

Parameter	**BA (Batch Extraction)**		**HBA (Batch Extraction)**		**Soil (Batch Extraction)**		**5%BA (Batch Extraction)**		**5%HBA (Batch Extraction)**	
	Mean	*SD*	*Mean*	*SD*	*Mean*	*SD*	*Mean*	*SD*	*Mean*	*SD*
Sb (ppm)	<12	<12	<12	<12	<12	<12	<12	<12	<12	<12
Sn (ppm)	8.90	0.20	7.01	0.45	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0
Sr (ppm)	442	22	413	17	210	2	220	3	212	4
Ti (ppm)	2272	109	2260	78	5149	42	5056	78	4987	92
Tl (ppm)	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0
U (ppm)	<60	<60	<60	<60	<60	<60	<60	<60	<60	<60
V (ppm)	63.1	2.2	62.8	3.9	114	0	110	1	108	1
W (ppm)	198	26	153	10	44.6	3.4	48.3	4.8	46.1	5.6
Y (ppm)	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0
Zn (ppm)	133	27	104	6	142	1	143	4	134	2
Zr (ppm)	56.7	3.6	55.0	1.2	91.0	4.3	91.4	1.3	86.0	1.5

Table A1.5 – Total loss of individual elements (%) from original concentration amounts as calculated from ICP solid phase analysis ($HNO_3/HF/H_2BO_3$ digestion) and ICP aqueous phase analysis.

Parameter (%)	BA	HBA	Soil	5%BA	5%HBA
	Mean	*Mean*	*Mean*	*Mean*	*Mean*
Ag	n/a	n/a	n/a	n/a	n/a
Al	2.52	1.21	0.14	0.30	0.27
As	n/a	n/a	n/a	n/a	n/a
Ba	10.43	7.76	0.20	0.39	1.41
Be	n/a	n/a	n/a	n/a	n/a
Bi	n/a	n/a	n/a	n/a	n/a
Ca	22.57	10.76	0.88	11.03	14.57
Cd	n/a	n/a	n/a	n/a	n/a
Co	0.01	0.01	0.69	0.60	0.64
Cr	6.22	6.35	0.28	0.45	0.77
Cu	2.60	0.19	0.99	1.93	1.61
Fe	0.0041	0.0021	0.57	0.46	0.49
Hg	n/a	n/a	n/a	n/a	n/a
K	10.30	12.12	0.56	1.54	2.30
Li	1.48	1.87	0.12	0.09	0.11
Mg	0.32	0.60	0.67	2.23	3.20
Mn	0.00401	0.00313	1.44	1.31	1.35
Mo	58.98	41.18	n/a	n/a	n/a
Na	3.92	4.06	0.19	0.30	0.53
Ni	0.05	0.04	0.53	0.70	0.64
P	0.43	0.48	1.93	6.19	5.83
Pb	n/a	n/a	n/a	n/a	n/a
S**	36.5	25.1	145	89.1	61.1
Sb	n/a	n/a	n/a	n/a	n/a
Sn	0.25	0.21	n/a	n/a	n/a
Sr	19.90	12.10	0.40	2.89	4.16
Ti	0.00198	0.00200	0.07	0.07	0.07
Tl	n/a	n/a	n/a	n/a	n/a
U	n/a	n/a	n/a	n/a	n/a
V	5.41	4.45	0.47	0.86	0.88
W	7.01	8.30	0.08	3.08	5.42
Y	n/a	n/a	n/a	n/a	n/a
Zn	0.39	0.27	0.65	0.58	0.60
Zr	n/a	n/a	0.05	0.07	0.06

**n/a refers to below detection limit*
***Percent loss based on solid phase data*

Table A1.6 – Anion concentration of bottom ash leachates from serial batch extraction during days one, ten and twenty; n=4.

Parameter	**Day 1**		**Day 10**		**Day 20**	
	Mean	*SD*	*Mean*	*SD*	*Mean*	*SD*
Br (ppm)	<0.01	n/a	<0.01	n/a	<0.01	n/a
Cl (ppm)	7.04	0.28	1.80	1.20	0.45	0.95
F (ppm)	0.49	0.02	0.02	0.00	<0.01	n/a
NO2 (ppm)	1.13	0.02	<0.01	n/a	<0.01	n/a
NO3 (ppm)	3.55	0.09	0.44	0.27	0.32	0.11
PO4 (ppm)	<0.01	n/a	<0.01	n/a	<0.01	n/a
SO4 (ppm)	5.36	0.67	1.39	0.12	2.41	0.10
Alkalinity (mg L^{-})	1617	60	133.0	38.0	67.16	2.01

**Alkalinity as $CaCO_3$*

Table A1.7 – Anion concentration of hardened bottom ash leachates from serial batch extraction during days one, ten and twenty; n=4.

Parameter	**Day 1**		**Day 10**		**Day 20**	
	Mean	*SD*	*Mean*	*SD*	*Mean*	*SD*
Br (ppm)	<0.01	n/a	<0.01	n/a	<0.01	n/a
Cl (ppm)	5.30	1.16	2.37	0.06	0.03	0.03
F (ppm)	0.39	0.00	0.01	0.00	<0.01	n/a
NO2 (ppm)	1.11	0.01	<0.01	n/a	<0.01	n/a
NO3 (ppm)	2.96	0.08	2.21	3.11	3.27	5.54
PO4 (ppm)	<0.01	n/a	<0.01	n/a	<0.01	n/a
SO4 (ppm)	47.47	2.88	1.51	0.10	0.74	0.04
Alkalinity (mg L^{-})	187.0	17.9	77.88	5.99	48.34	4.00

**Alkalinity as $CaCO_3$*

Table A1.8 – Anion concentration of soil leachates from serial batch extraction during days one, ten and twenty; n=4.

Parameter	**Day 1**		**Day 10**		**Day 20**	
	Mean	*SD*	*Mean*	*SD*	*Mean*	*SD*
Br (ppm)	<0.01	n/a	<0.01	n/a	<0.01	n/a
Cl (ppm)	1.17	1.28	2.36	0.08	0.57	1.04
F (ppm)	0.32	0.01	0.01	0.00	<0.01	n/a
NO2 (ppm)	0.99	0.01	<0.01	n/a	<0.01	n/a
NO3 (ppm)	5.15	0.27	0.50	0.08	0.54	0.35
PO4 (ppm)	<0.01	n/a	1.07	0.01	0.89	0.01
SO4 (ppm)	0.24	0.03	0.03	0.01	<0.01	n/a
Alkalinity (mg L^{-})	2.73	1.87	0.39	0.35	1.27	n/a

**Alkalinity as $CaCO_3$*

Table A1.9 – Anion concentration of soil with 5% bottom ash leachates from serial batch extraction during days one, ten and twenty; n=4.

Parameter	**Day 1**		**Day 10**		**Day 20**	
	Mean	*SD*	*Mean*	*SD*	*Mean*	*SD*
Br (ppm)	<0.01	n/a	<0.01	n/a	<0.01	n/a
Cl (ppm)	0.36	0.02	1.87	1.23	2.09	0.08
F (ppm)	0.46	0.01	<0.01	n/a	<0.01	n/a
NO2 (ppm)	1.07	0.01	0.81	0.01	0.92	0.01
NO3 (ppm)	5.32	0.03	0.31	0.17	0.33	0.02
PO4 (ppm)	1.38	0.08	1.38	0.06	1.13	0.04
SO4 (ppm)	5.80	0.40	0.07	0.02	<0.01	n/a
Alkalinity (mg L^{-})	31.34	1.84	12.63	3.82	5.47	0.77

**Alkalinity as* $CaCO_3$

Table A1.10 – Anion concentration of soil with 5% hardened bottom ash leachates from serial batch extraction during days one, ten and twenty; n=4.

Parameter	**Day 1**		**Day 10**		**Day 20**	
	Mean	*SD*	*Mean*	*SD*	*Mean*	*SD*
Br (ppm)	<0.01	n/a	<0.01	n/a	<0.01	n/a
Cl (ppm)	0.54	0.46	2.41	0.16	2.14	0.07
F (ppm)	0.40	0.01	<0.01	n/a	<0.01	n/a
NO2 (ppm)	1.11	0.03	0.80	0.01	0.94	0.02
NO3 (ppm)	5.02	0.25	0.41	0.03	0.30	0.08
PO4 (ppm)	<0.01	n/a	1.53	0.13	1.18	0.11
SO4 (ppm)	4.41	0.33	0.05	0.00	0.02	n/a
Alkalinity (mg L^{-})	69.46	1.67	8.16	3.35	4.41	0.60

**Alkalinity as* $CaCO_3$

Table A1.11 – Total elemental content present within the aqueous phase of the blank samples run during serial batch extraction.

Parameter	**Serial Batch Extraction Blanks**	
	Mean	*SD*
Ag (ppm)	2.64E-03	3.08E-03
Al (ppm)	8.23E-04	2.24E-04
As (ppm)	1.26E-05	1.06E-05
B (ppm)	1.06E-03	1.16E-03
Ba (ppm)	4.29E-04	5.32E-04
Be (ppb)	<1.0	n/a
Bi (ppm)	6.19E-06	8.07E-07
Ca (ppm)	4.70E-02	1.96E-02
Cd (ppm)	1.57E-05	7.20E-06
Co (ppb)	<0.1	n/a
Cr (ppb)	<0.1	n/a
Cu (ppm)	1.71E-04	5.16E-05
Fe (ppm)	5.10E-04	7.64E-04
Hg (ppm)	2.29E-06	2.04E-05
K (ppm)	1.03E-02	7.66E-03
Li (ppm)	1.25E-04	4.92E-05
Mg (ppm)	1.18E-03	9.03E-04
Mn (ppm)	1.57E-04	1.65E-04
Mo (ppm)	3.87E-05	3.12E-05
Na (ppm)	8.09E-03	1.40E-02
Ni (ppm)	9.46E-04	1.54E-03
P (ppm)	3.33E-03	1.86E-03
Pb (ppm)	1.55E-05	6.47E-06
Sb (ppm)	2.81E-06	1.81E-06
Se (ppm)	9.39E-05	5.29E-06
Si (ppb)	<1.0	n/a
Sn (ppb)	<0.1	n/a
Sr (ppm)	6.32E-05	2.16E-05
Te (ppb)	<0.1	n/a
Th (ppm)	9.65E-06	4.89E-06
Ti (ppb)	<0.1	n/a
Tl (ppm)	1.51E-05	7.69E-06
U (ppm)	1.13E-05	3.36E-06
V (ppm)	6.59E-05	8.20E-06
W (ppm)	4.07E-05	2.03E-05
Y (ppb)	<0.1	n/a
Zn (ppm)	2.94E-04	2.23E-04
Zr (ppb)	<0.1	n/a

Table A1.12 – Relative percent difference, RPD, calculation for TILL 3 standard as determined by ICP-OES following HCl/HNO3 digestion.

Parameter	**TILL 3 (As Measured by EPA Method 3051A)**	**TILL 3****	**RPD (%)**
	Mean		
Ag (ppm)	<1.0		
Al (%)	1.40	1.2	15.1
As (ppm)	86.9		
B (ppm)	8.07		
Ba (ppm)	57.7	49.2	15.9
Be (ppm)	<1.0	<2.0	
Bi (ppm)	<1.0		
Ca (%)	0.725		
Cd (ppm)	<1.0	<0.35	
Co (ppm)	30.9	14.8	70.5
Cr (ppm)	75.5		
Cu (ppm)	19.0	16.5	14.1
Fe (%)	2.06	2.1	2.1
Hg (ppm)	<2.0		
K (%)	0.192	0.0964	66.3
Li (ppm)	28.4		
Mg (%)	0.644	0.7445	14.5
Mn (%)	0.034	0.0317	5.8
Mo (ppm)	<1.0	6	
Na (%)	0.048	0.0427	11.5
Ni (ppm)	33.6	26.5	23.5
P (%)	0.051	0.0457	10.5
Pb (ppm)	13.0	23	55.9
S (%)	0.015		
Sb (ppm)	<4.0		
Sn (ppm)	<1.0		
Sr (ppm)	46.1		
Ti (ppm)	1344		
Tl (ppm)	<2.0		
U (ppm)	<20		
V (ppm)	53.3	66.1	21.5
Y (ppm)	<2.0		
Zn (ppm)	51.3	42.7	18.3
Zr (ppm)	15.4		

*EPA Method 3051A follows HCl/HNO3 digestion, and a relative percent difference, RPD, within 15% is considered good

**TILL 3 values obtained from TILL Certificate of Analysis, Single source data by EPA 3051 digestion

Table A1.13 – Relative percent difference, RPD, calculation for TILL 3 standard as determined by ICP-OES following HNO3/HF/H2BO3 digestion.

Parameter	**TILL 3 (As Measured by EPA Method 3052)**	**TILL 3****	**RPD (%)**
	Mean		
Ag (ppm)	<3.0		
Al (%)	6.65		
As (ppm)	<12	87	
Ba (ppm)	447	489	8.9
Be (ppm)	<3.0	2	
Bi (ppm)	<3.0	<5	
Ca (%)	1.92		
Cd (ppm)	<3.0		
Co (ppm)	32.5	15	73.6
Cr (ppm)	97.8	123	22.8
Cu (ppm)	22.2	22	0.9
Fe (%)	2.90	2.78	4.1
Hg (ppm)	<6.0		
K (%)	2.18		
Li (ppm)	24.5	21	15.4
Mg (%)	1.09		
Mn (%)	0.0518	0.052	0.4
Mo (ppm)	<3.0	2	
Na (%)	2.03		
Ni (ppm)	40.1	39	2.8
P (%)	0.0529	0.049	7.7
Pb (ppm)	16.9	26	42.4
S (%)	0.00306	<0.05	
Sb (ppm)	<12	0.9	
Sn (ppm)	<3.0		
Sr (ppm)	273	300	9.5
Ti (ppm)	2690	2910	7.9
Tl (ppm)	<6.0		
U (ppm)	<60	2.1	
V (ppm)	67.3	62	8.2
W (ppm)	167	<1	
Y (ppm)	<6.0	17	
Zn (ppm)	53	56	6.4
Zr (ppm)	129	230	56.2

*EPA Method 3052 follows HNO3/HF/H2BO3 digestion, and a relative percent difference, RPD, within 15% is considered good

**TILL 3 values obtained from TILL Certificate of Analysis, Summary of "total" elements in TILL series

APPENDIX A2

Serial Batch Extraction Graphs from ICP-MS Data; n=4

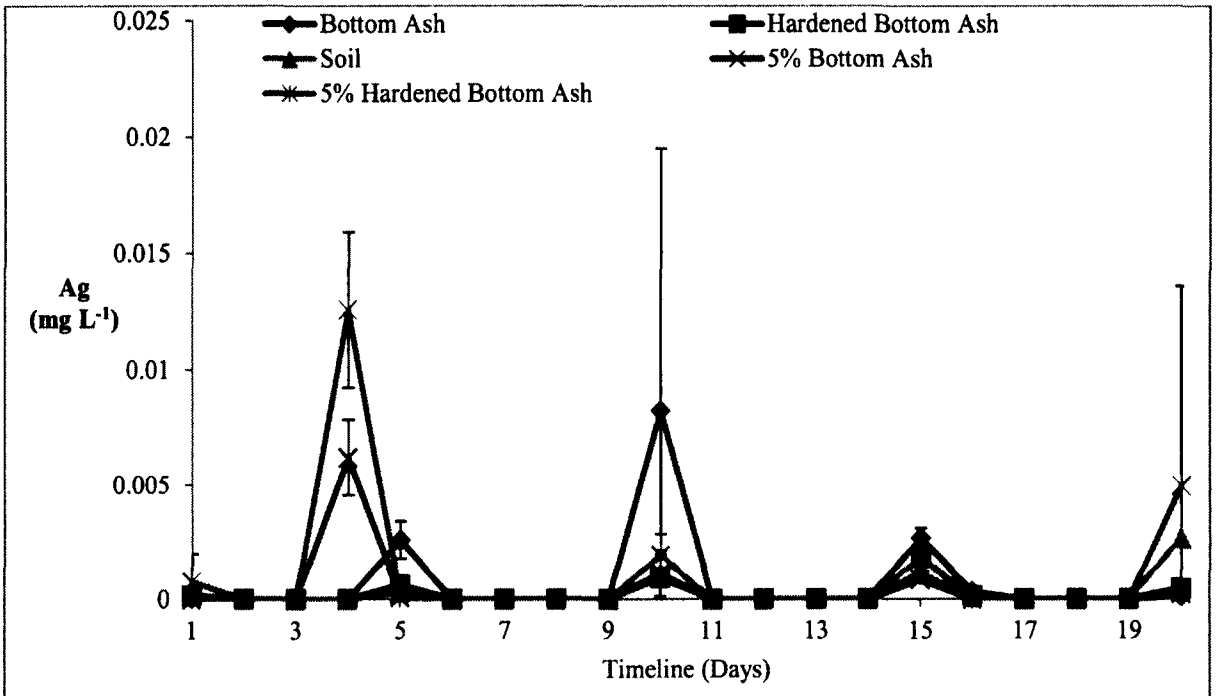

Figure A2.0 - Aqueous concentrations (with standard deviation error bars) for Ag (silver) during serial batch extraction.

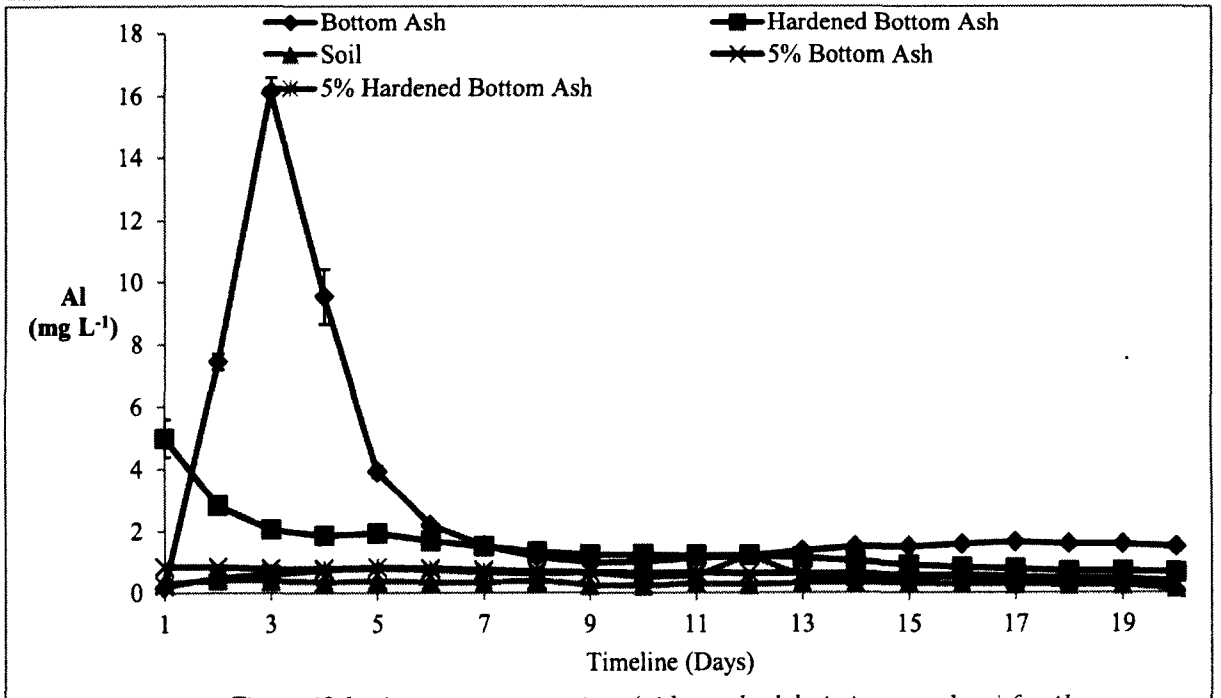

Figure A2.1 - Aqueous concentrations (with standard deviation error bars) for Al (aluminum) during serial batch extraction.

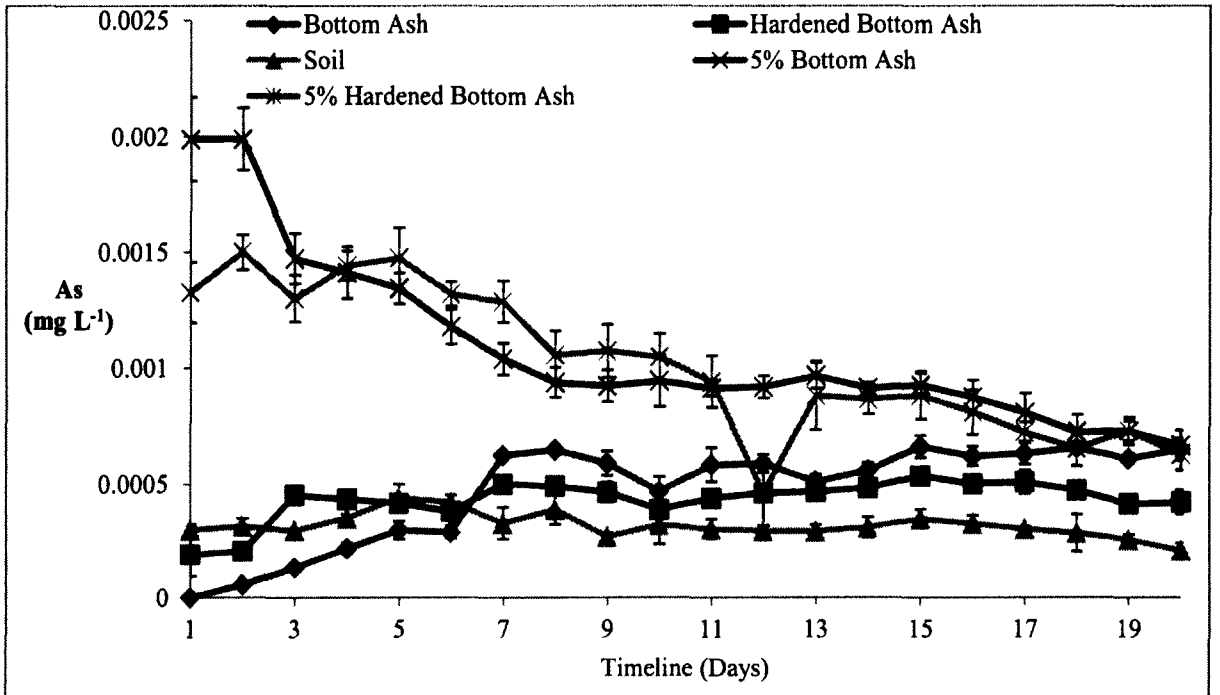

Figure A2.2 - Aqueous concentrations (with standard deviation error bars) for As (arsenic) during serial batch extraction.

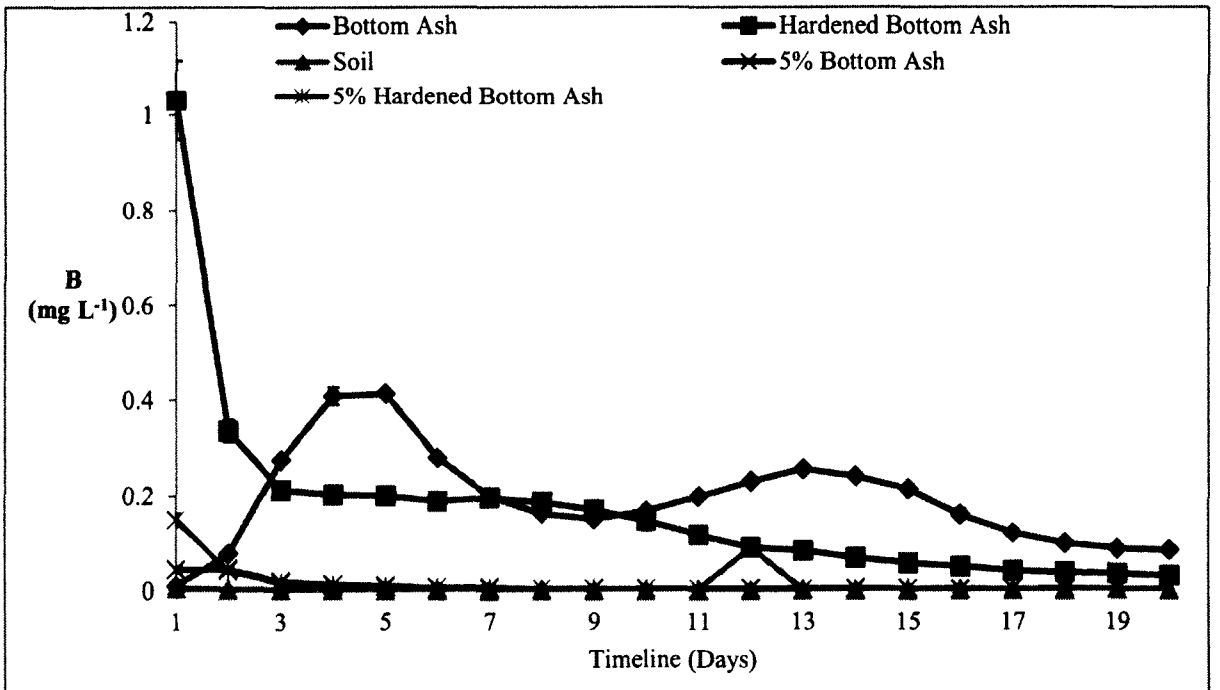

Figure A2.3 - Aqueous concentrations (with standard deviation error bars) for B (boron) during serial batch extraction.

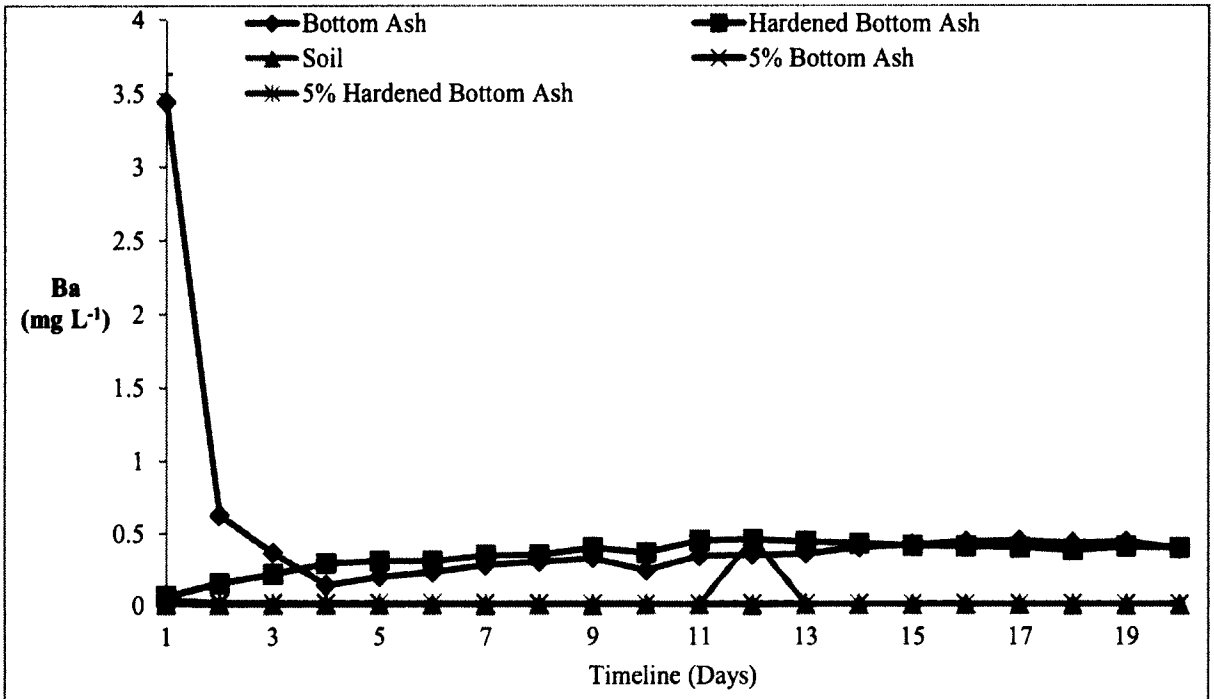

Figure A2.4 - Aqueous concentrations (with standard deviation error bars) for Ba (barium) during serial batch extraction.

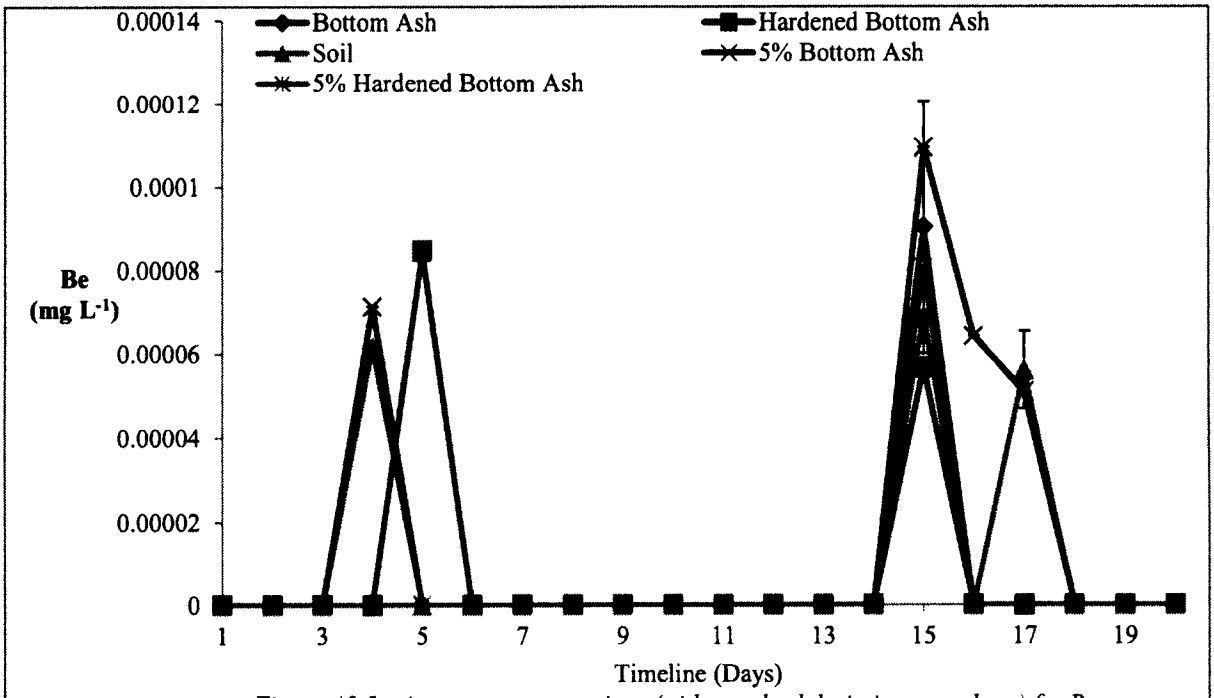

Figure A2.5 - Aqueous concentrations (with standard deviation error bars) for Be (beryllium) during serial batch extraction.

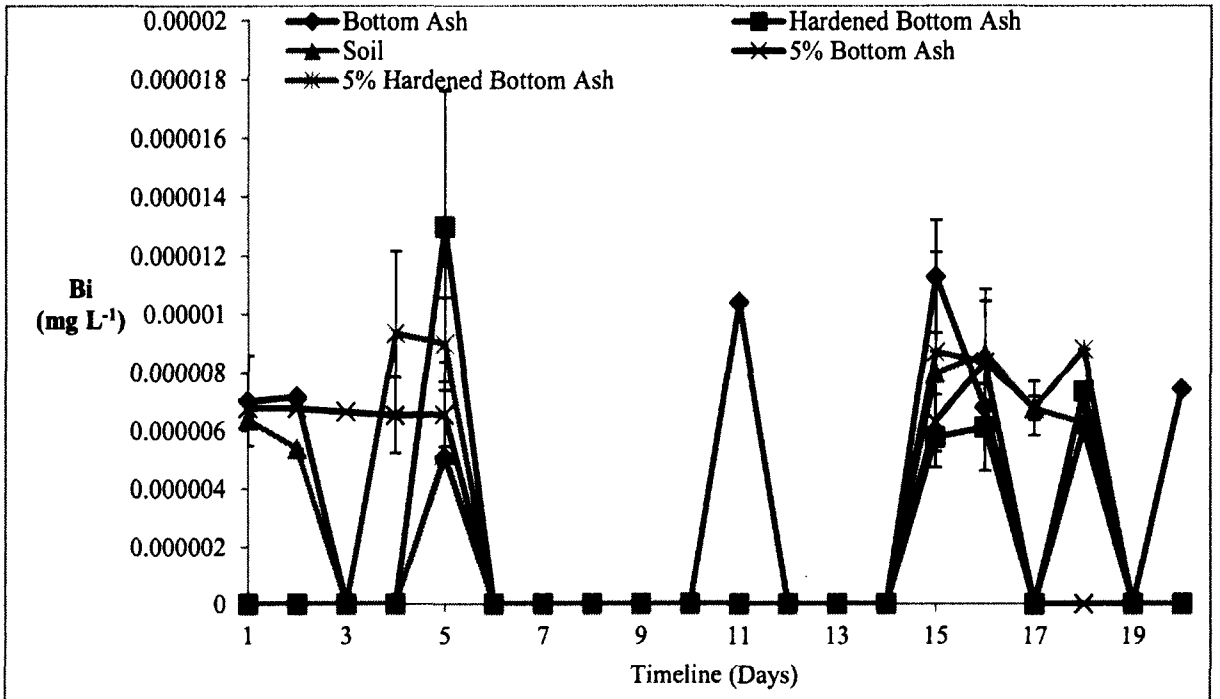

Figure A2.6 - Aqueous concentrations (with standard deviation error bars) for Bi (bismuth) during serial batch extraction.

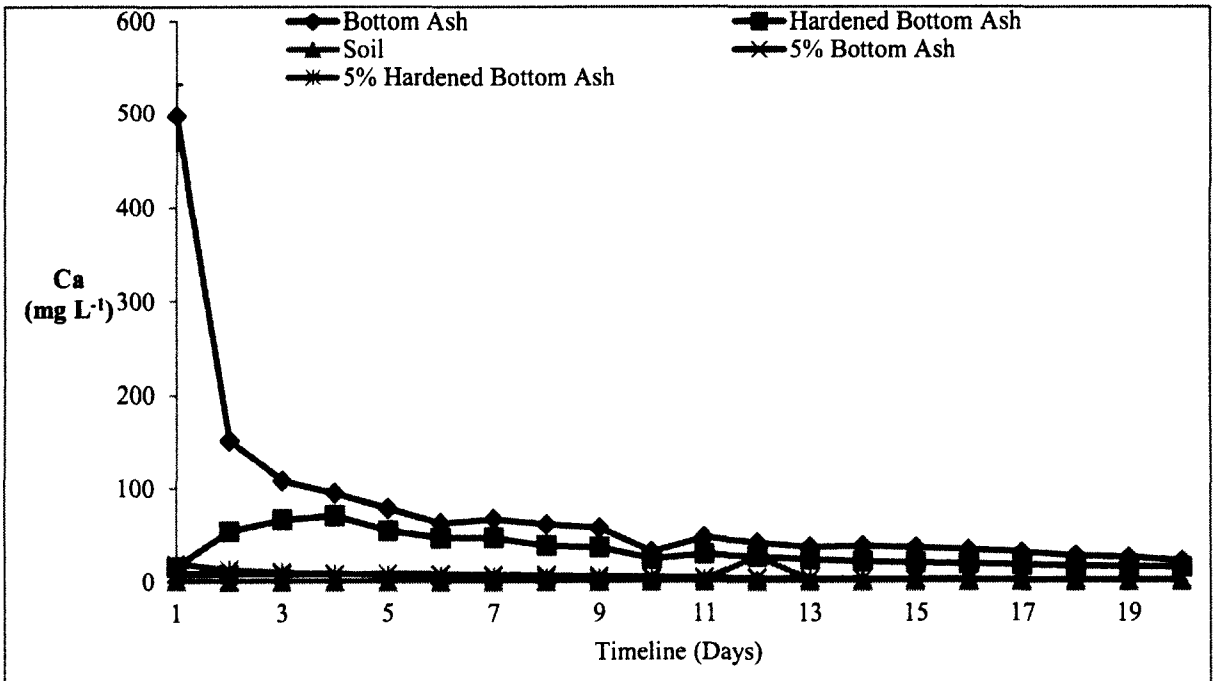

Figure A2.7 - Aqueous concentrations (with standard deviation error bars) for Ca (calcium) during serial batch extraction.

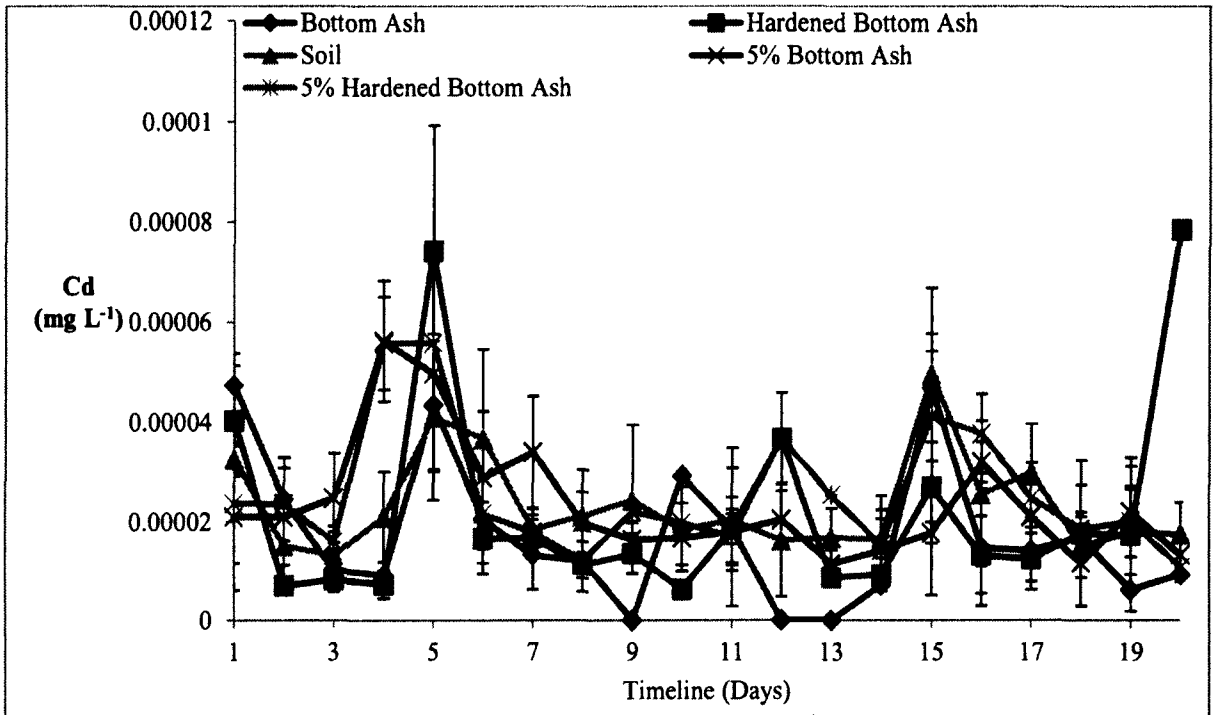

Figure A2.8 - Aqueous concentrations (with standard deviation error bars) for Cd (cadmium) during serial batch extraction.

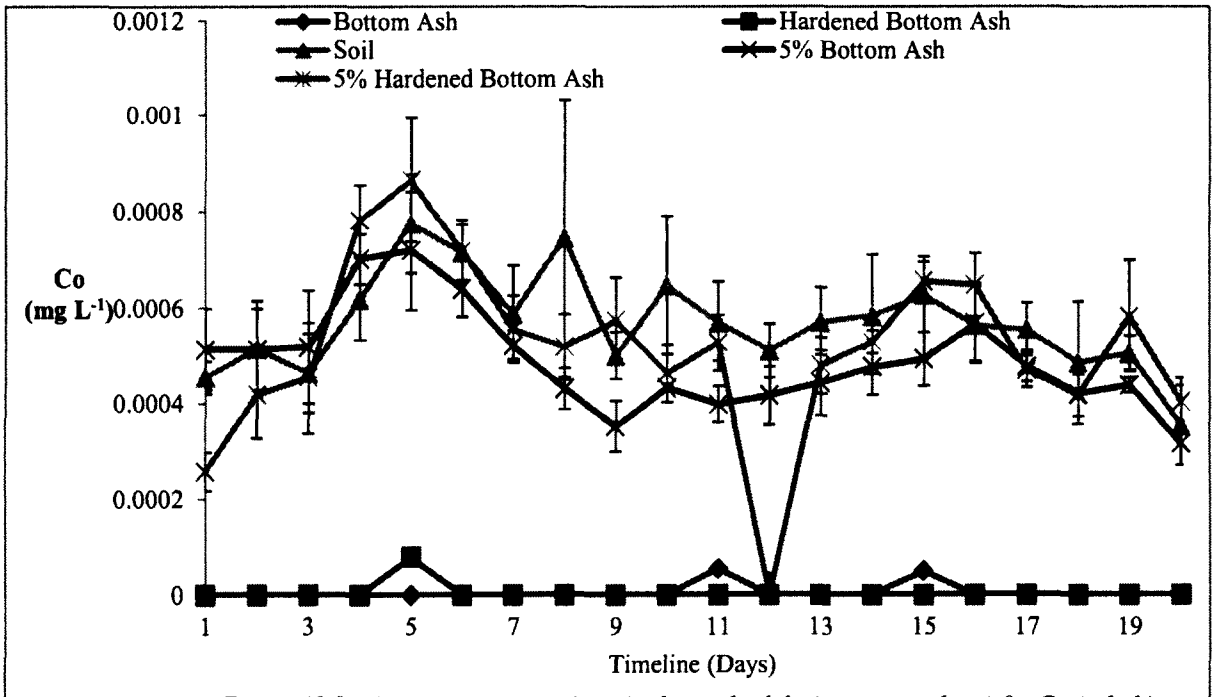

Figure A2.9 - Aqueous concentrations (with standard deviation error bars) for Co (cobalt) during serial batch extraction.

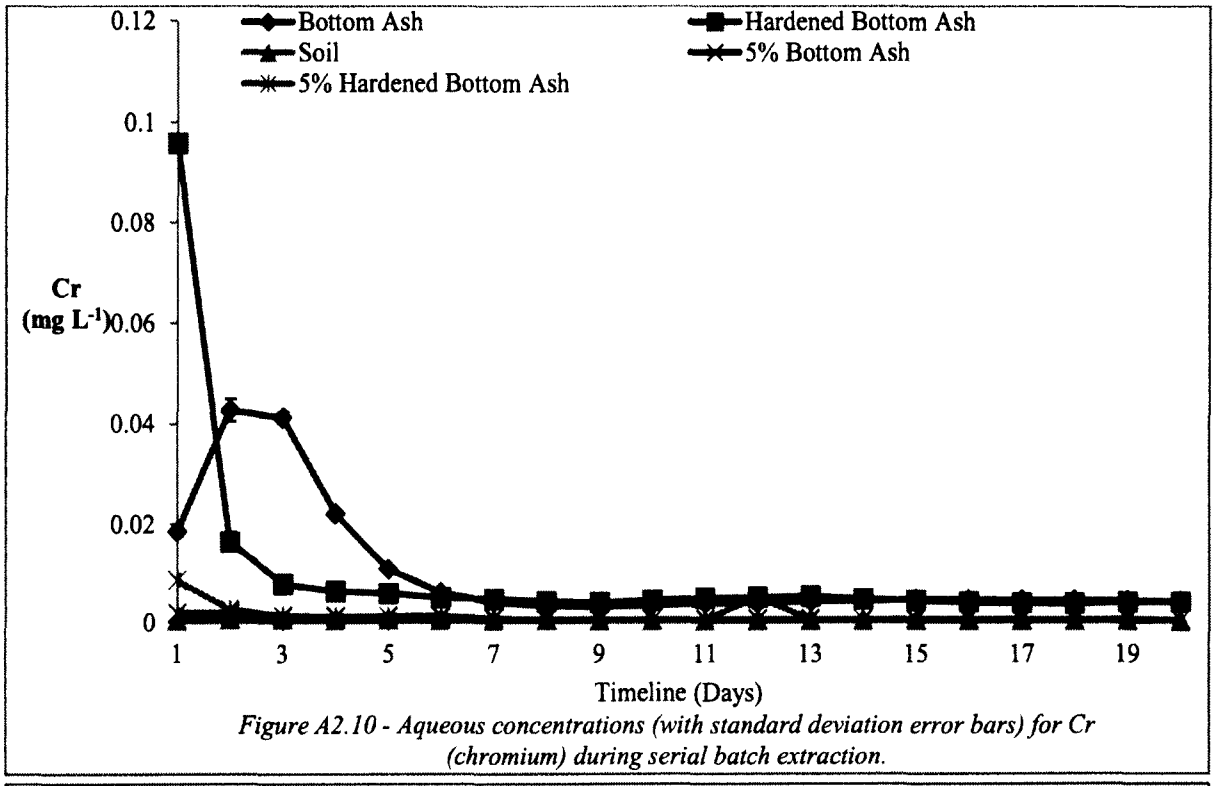

Figure A2.10 - Aqueous concentrations (with standard deviation error bars) for Cr (chromium) during serial batch extraction.

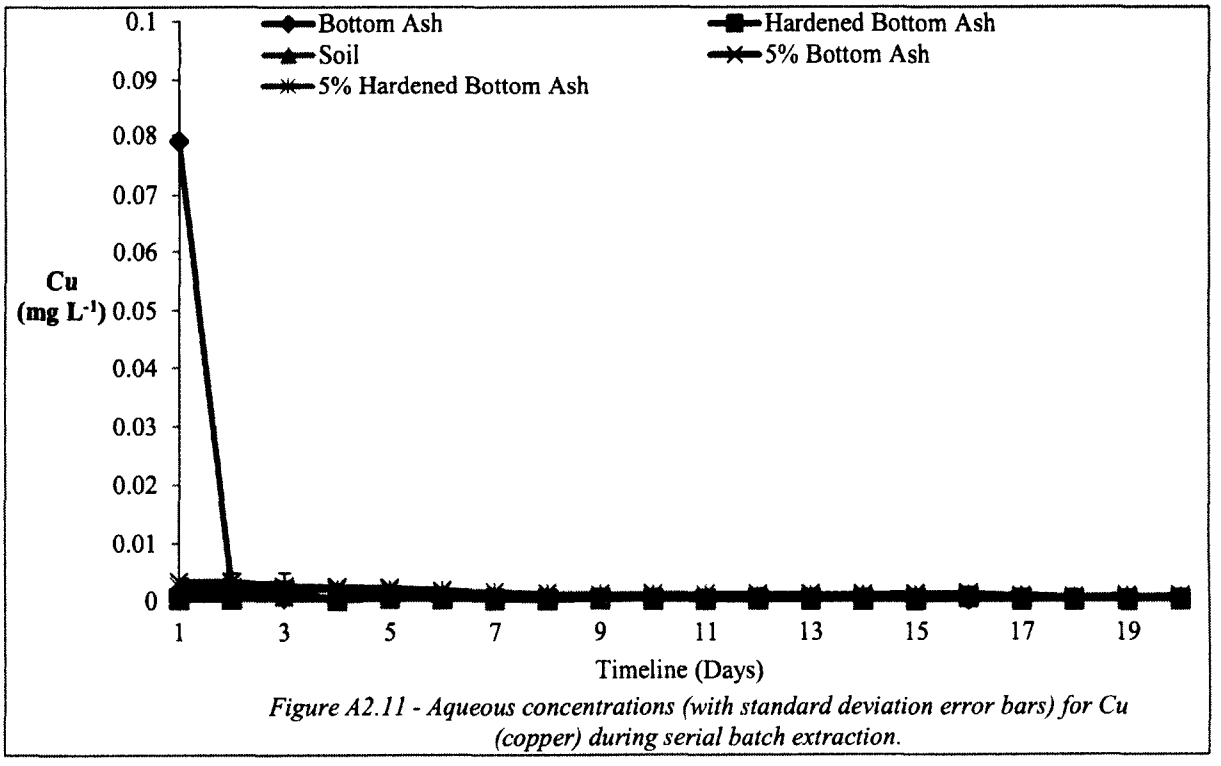

Figure A2.11 - Aqueous concentrations (with standard deviation error bars) for Cu (copper) during serial batch extraction.

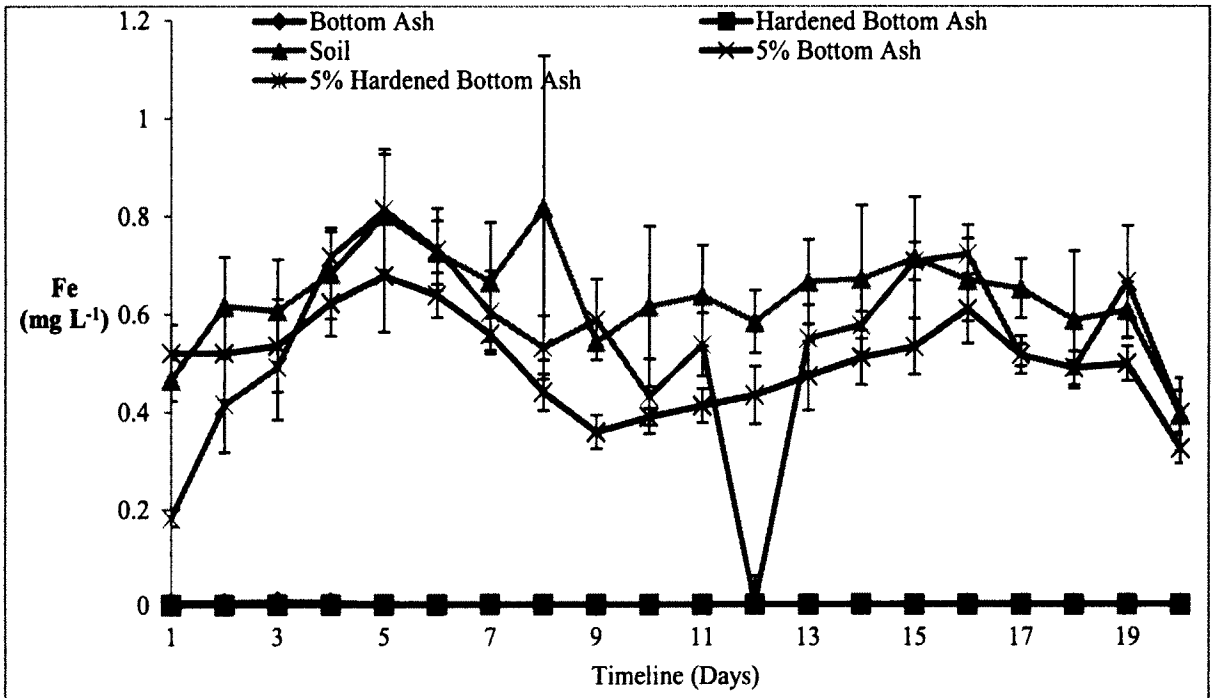

Figure A2.12 - Aqueous concentrations (with standard deviation error bars) for Fe (iron) during serial batch extraction.

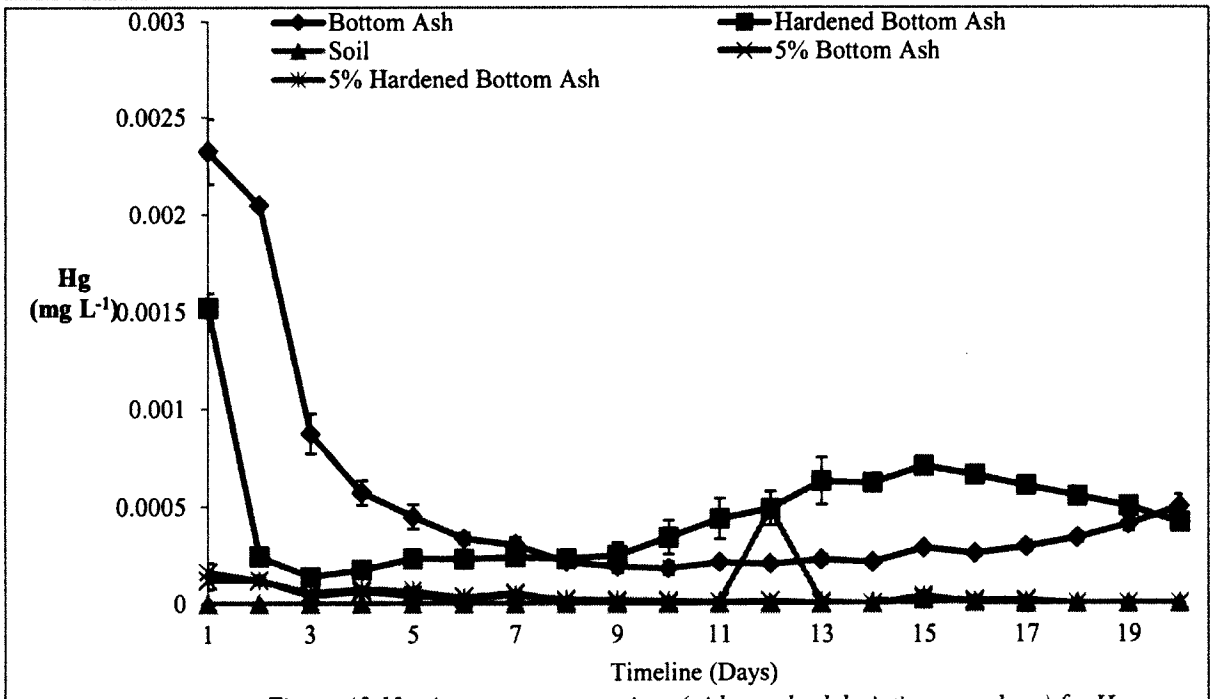

Figure A2.13 - Aqueous concentrations (with standard deviation error bars) for Hg (mercury) during serial batch extraction.

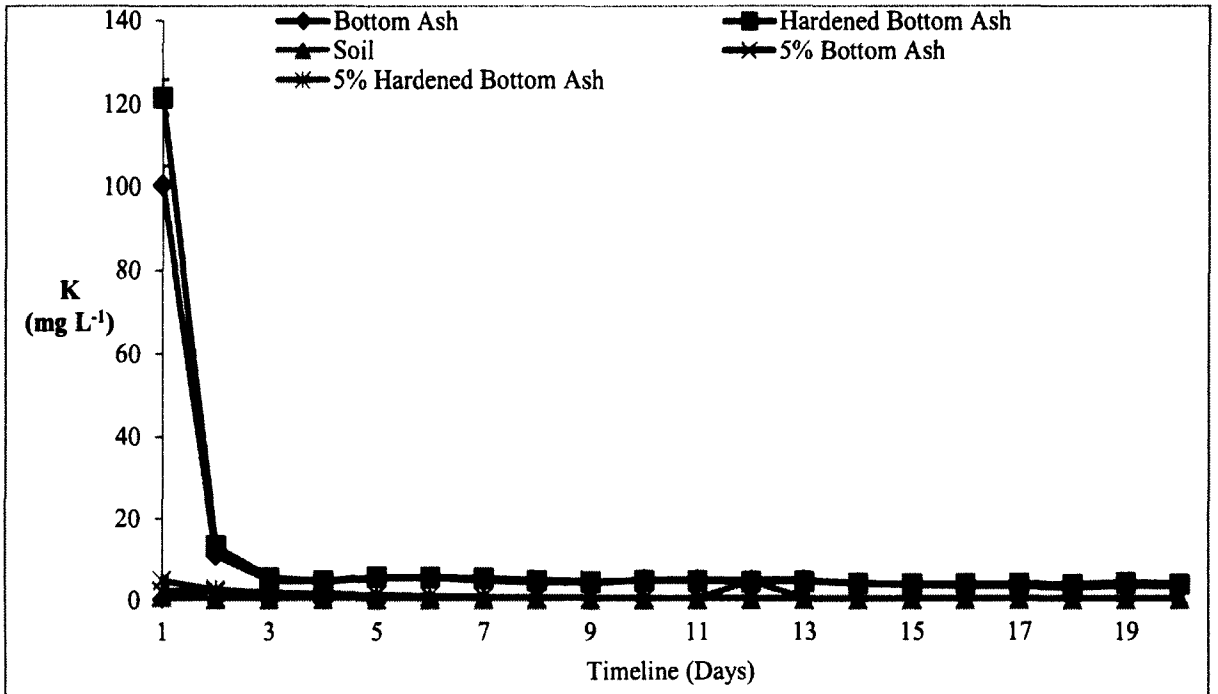

Figure A2.14 - Aqueous concentrations (with standard deviation error bars) for K (potassium) during serial batch extraction.

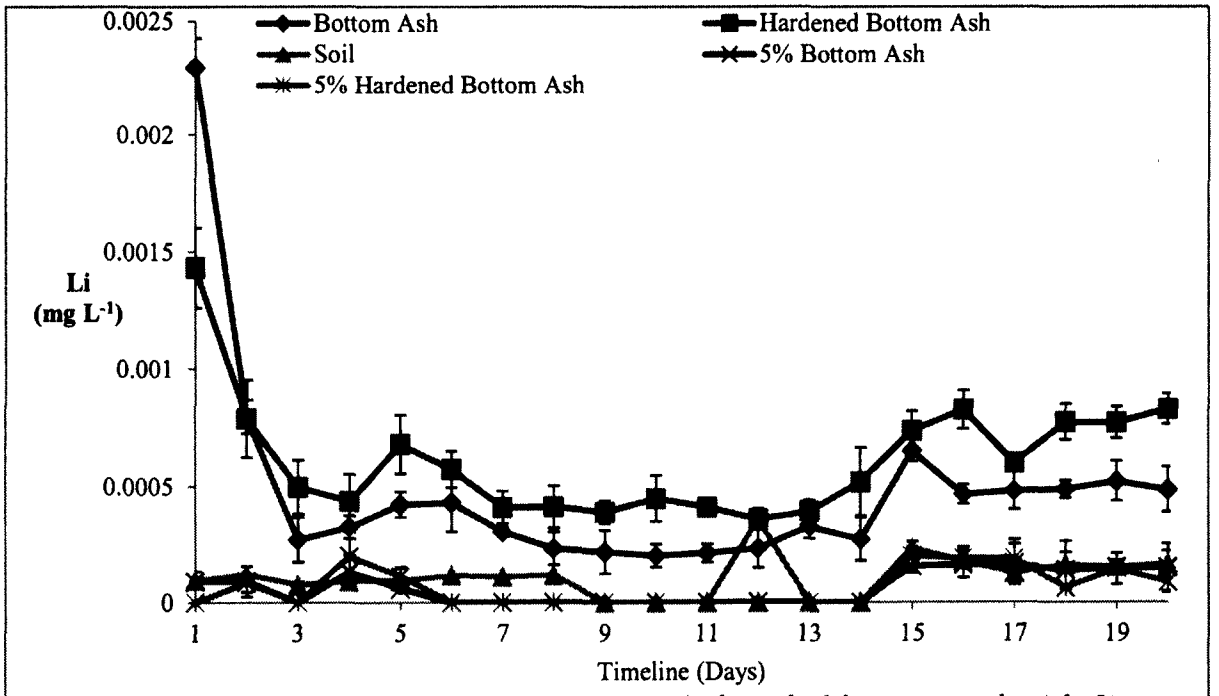

Figure A2.15 - Aqueous concentrations (with standard deviation error bars) for Li (lithium) during serial batch extraction.

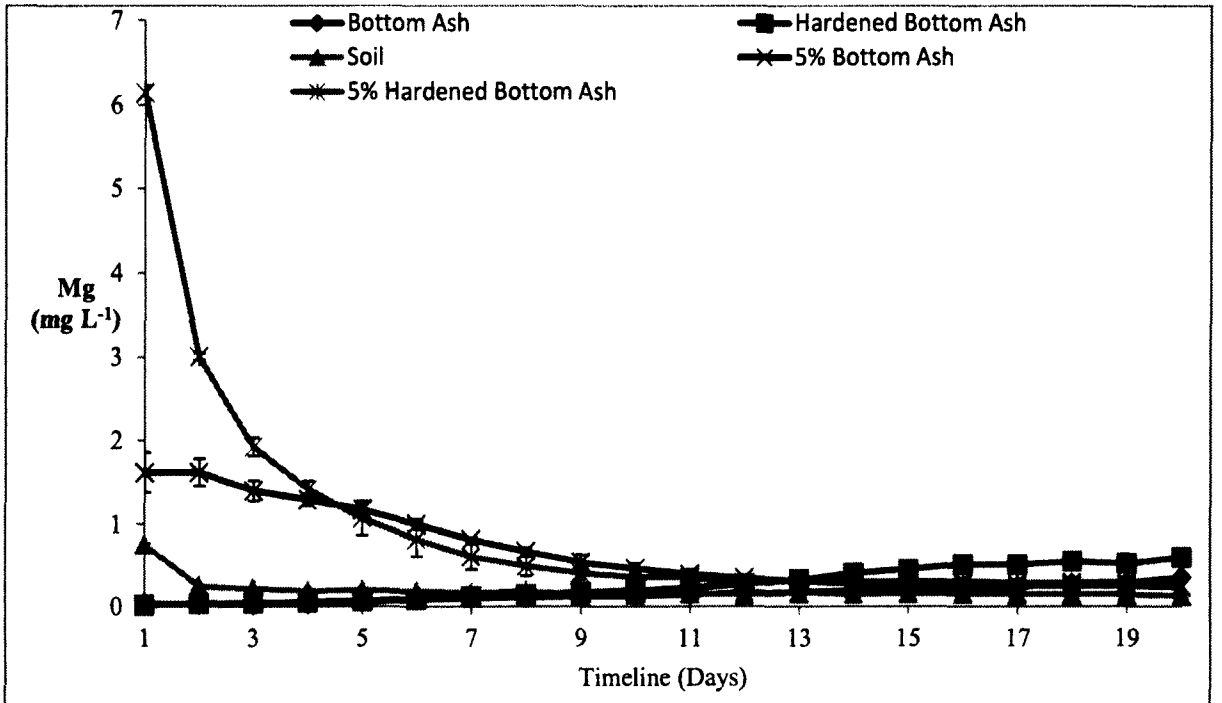

Figure A2.16 - Aqueous concentrations (with standard deviation error bars) for Mg (magnesium) during serial batch extraction.

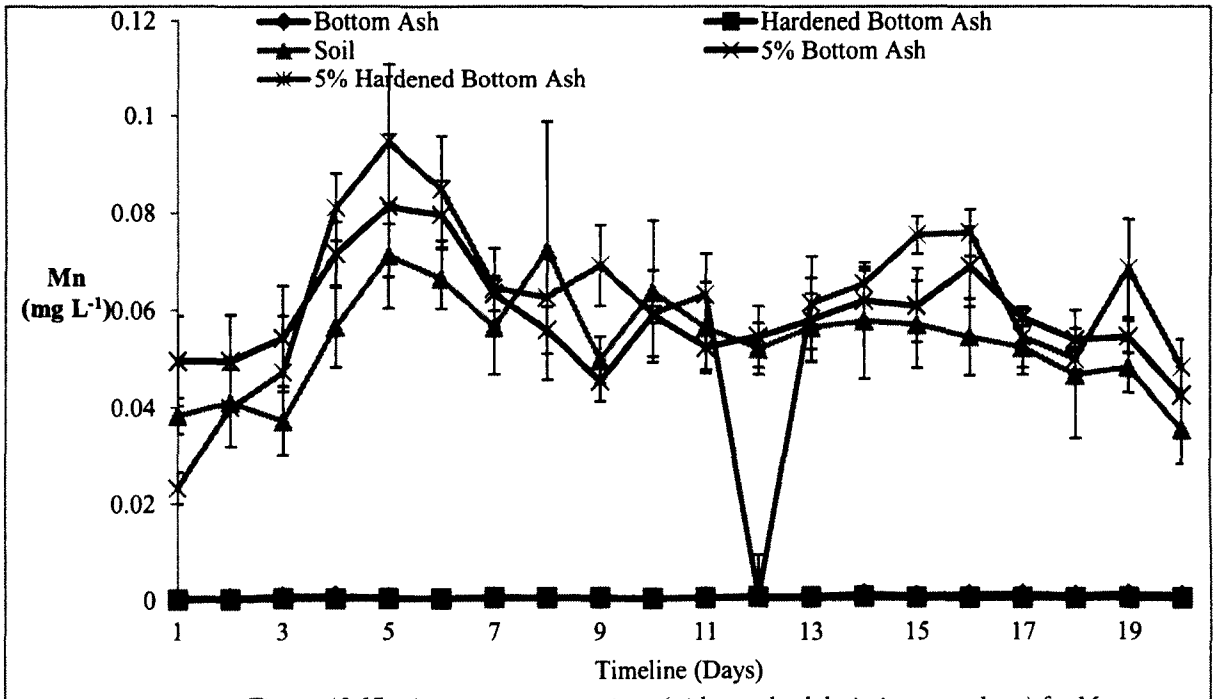

Figure A2.17 - Aqueous concentrations (with standard deviation error bars) for Mn (manganese) during serial batch extraction.

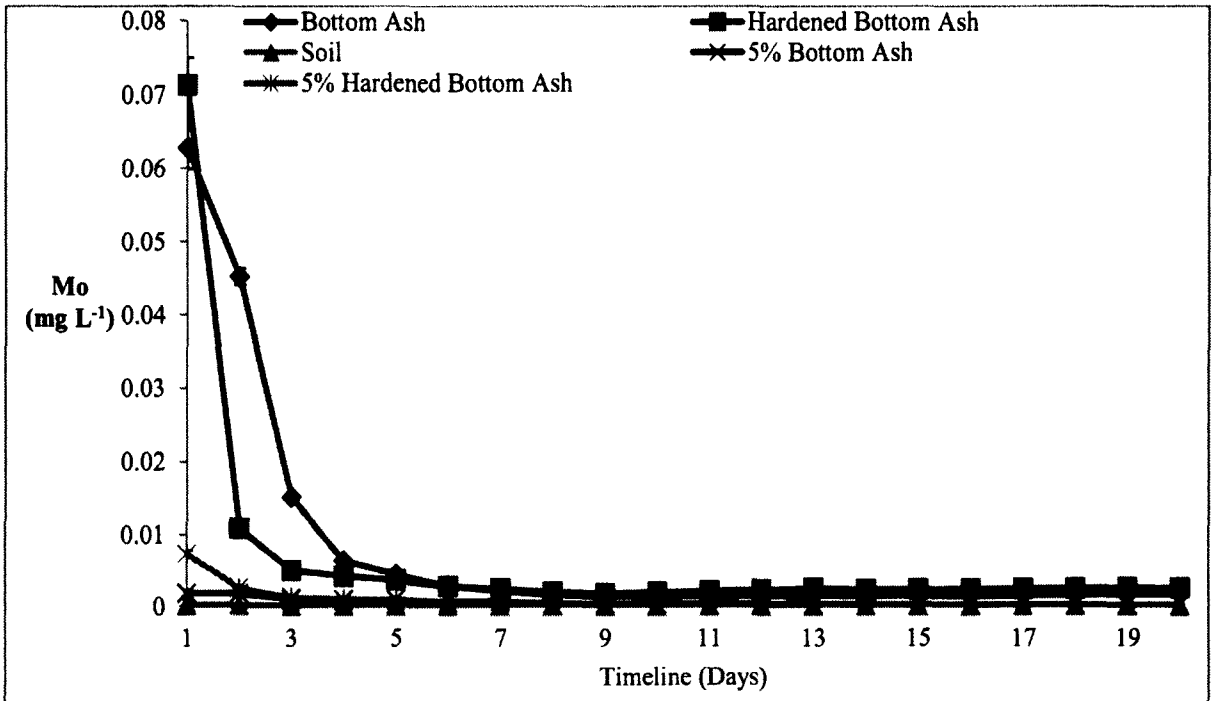

Figure A2.18 - Aqueous concentrations (with standard deviation error bars) for Mo (molybdenum) during serial batch extraction.

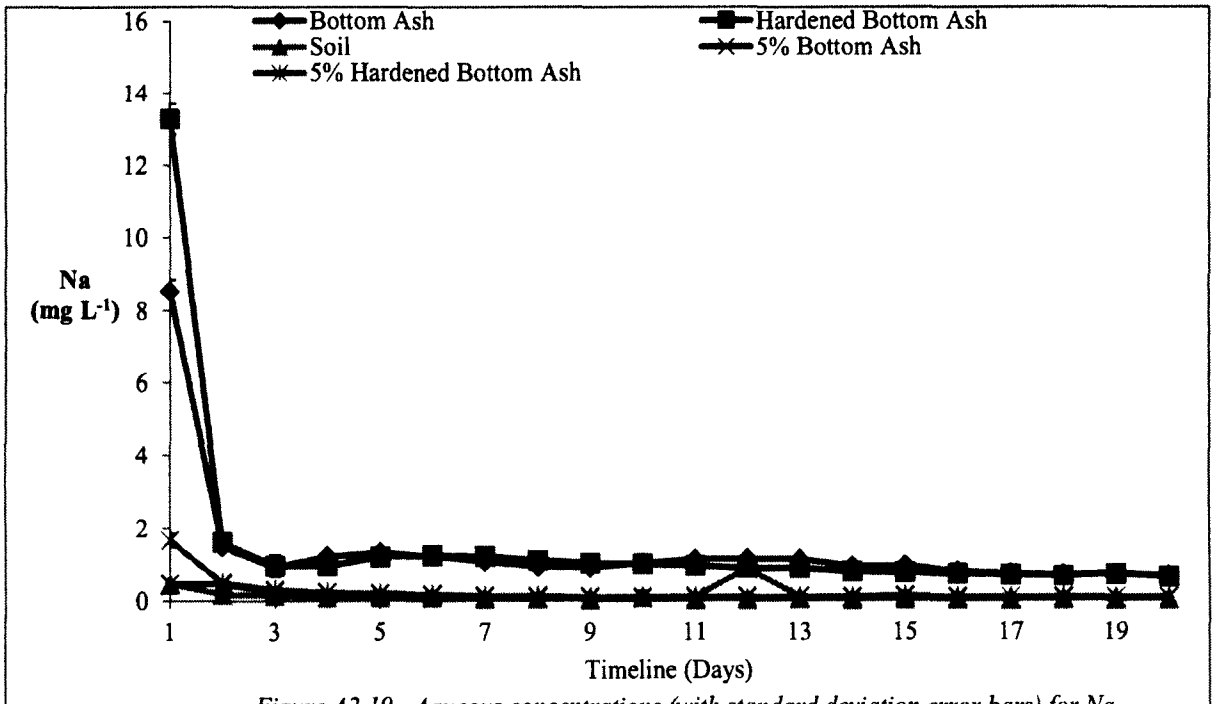

Figure A2.19 - Aqueous concentrations (with standard deviation error bars) for Na (sodium) during serial batch extraction.

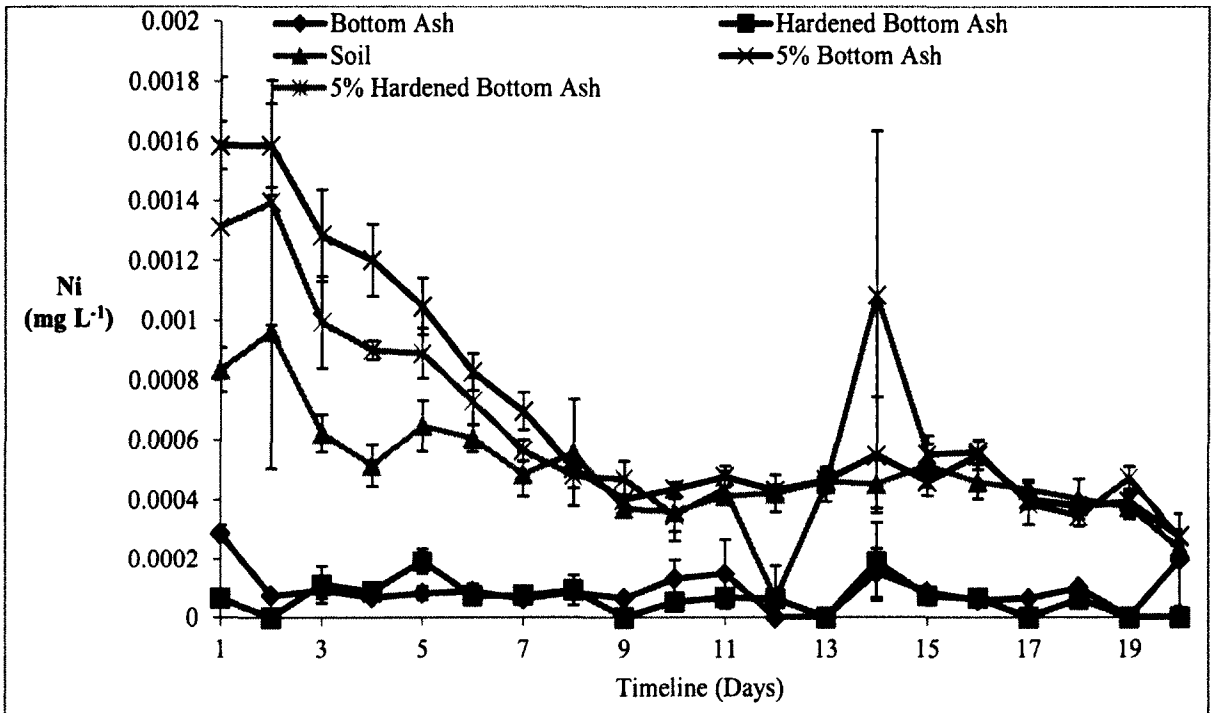

Figure A2.20 - Aqueous concentrations (with standard deviation error bars) for Ni (nickel) during serial batch extraction.

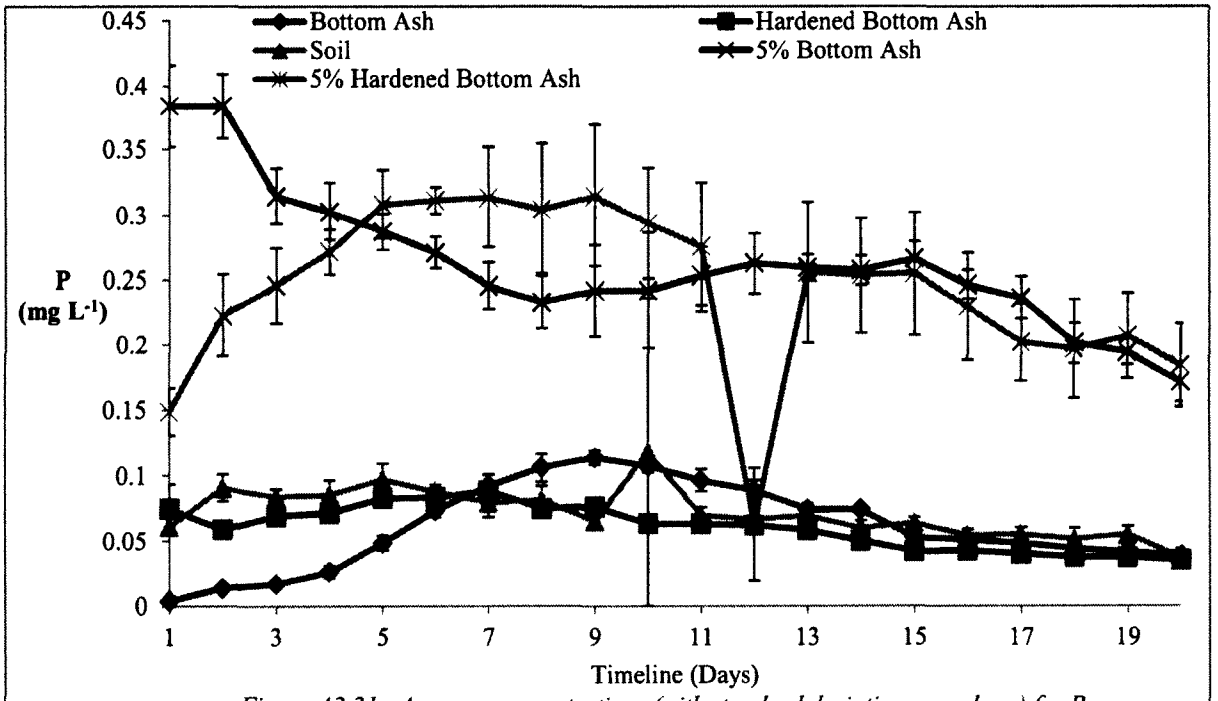

Figure A2.21 - Aqueous concentrations (with standard deviation error bars) for P (phosphorus) during serial batch extraction.

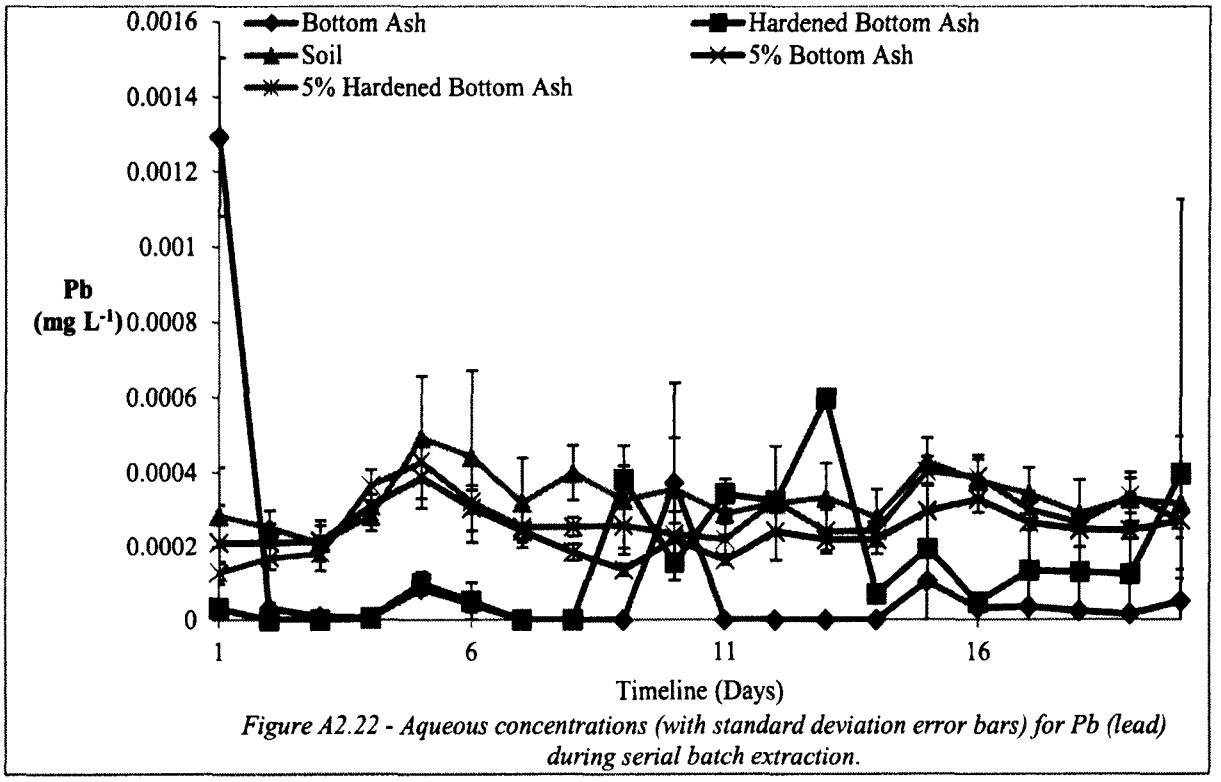

Figure A2.22 - Aqueous concentrations (with standard deviation error bars) for Pb (lead) during serial batch extraction.

-()

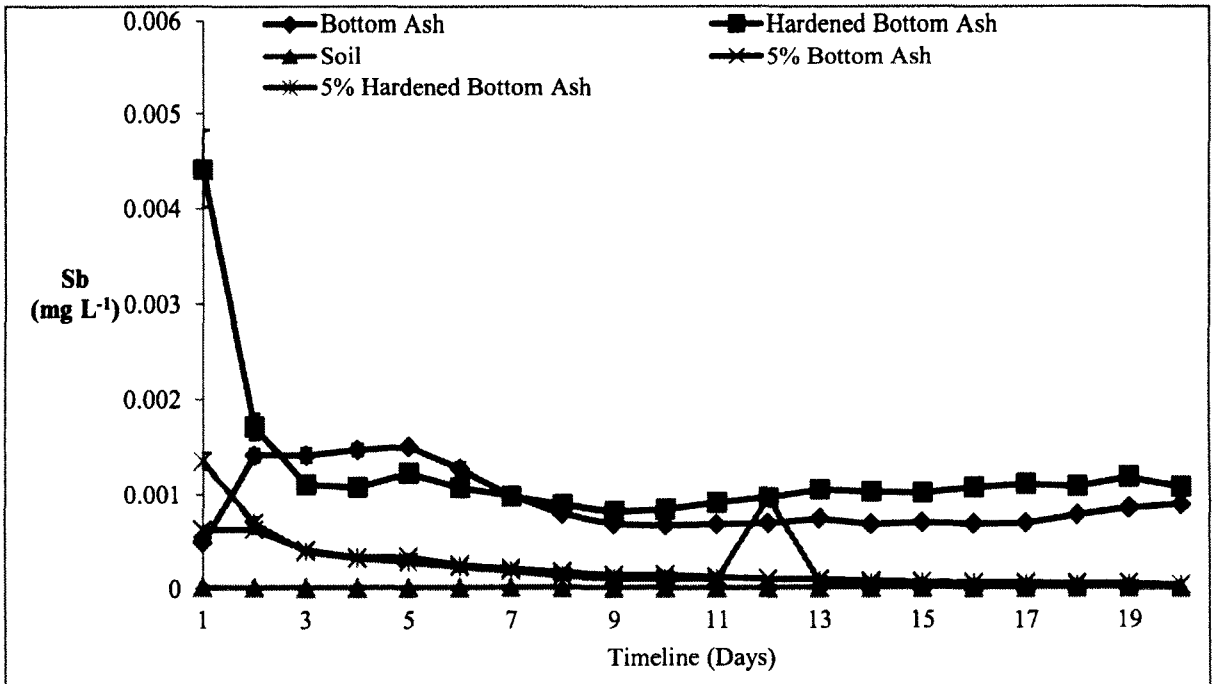

Figure A2.23 - Aqueous concentrations (with standard deviation error bars) for Sb (antimony) during serial batch extraction.

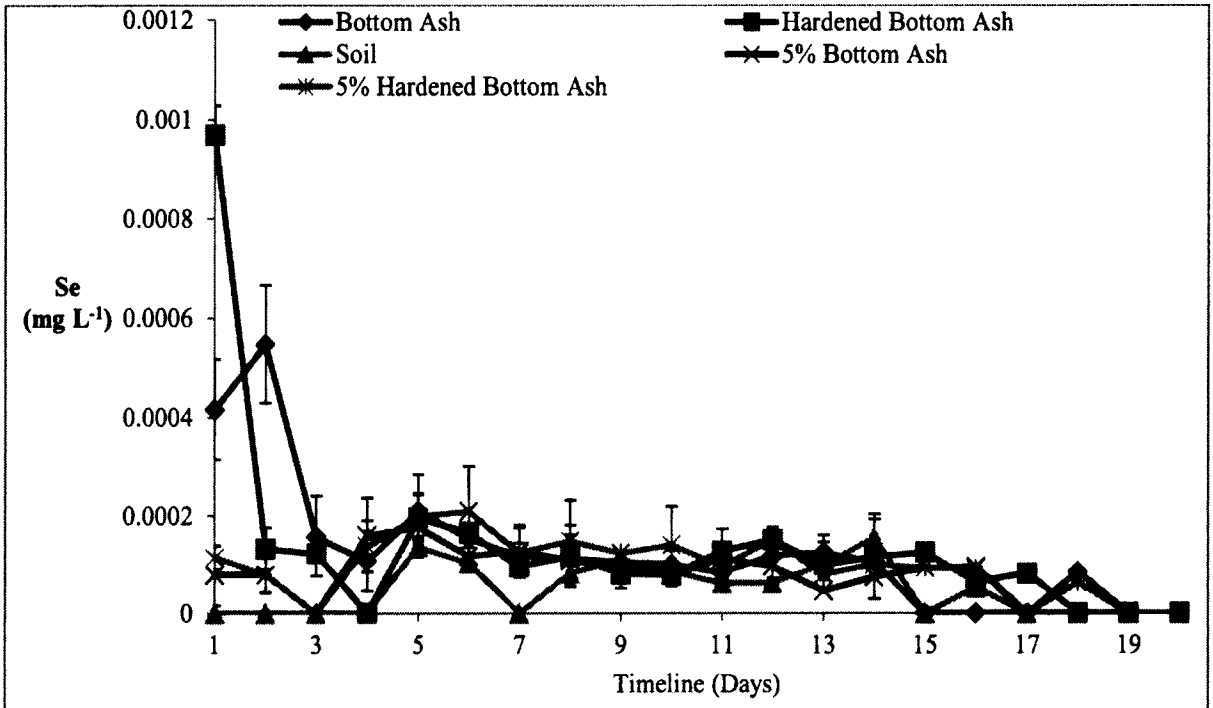

Figure A2.24 - Aqueous concentrations (with standard deviation error bars) for Se (selenium) during serial batch extraction.

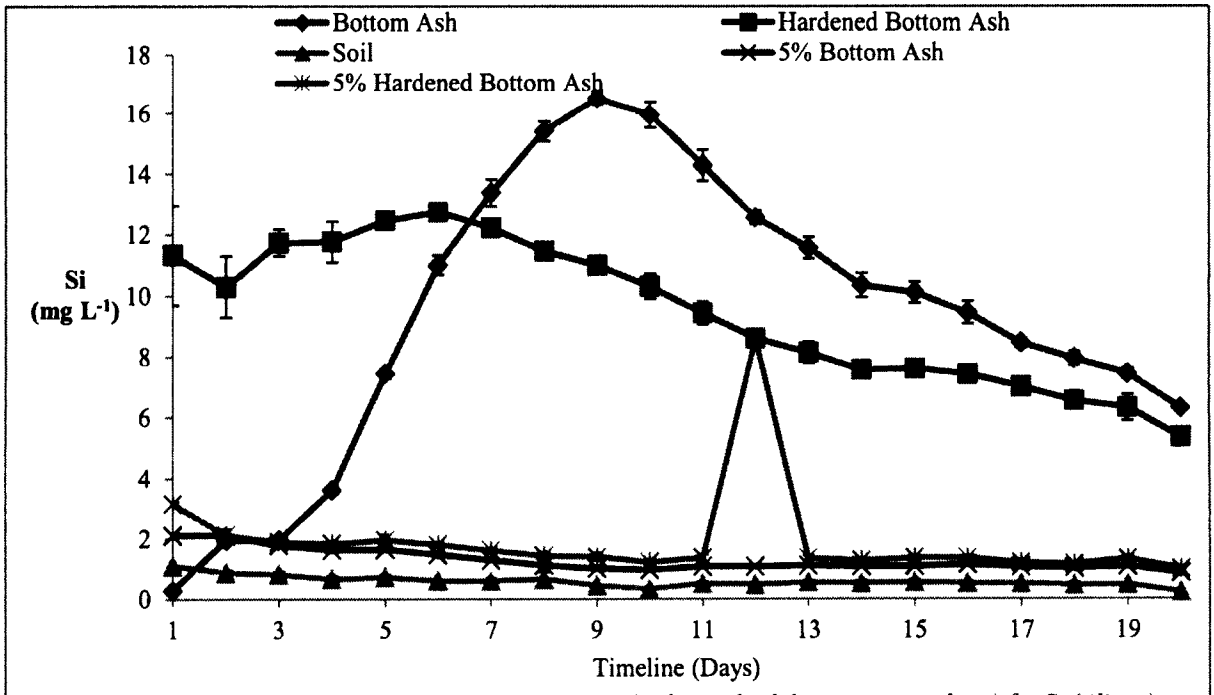

Figure A2.25 - Aqueous concentrations (with standard deviation error bars) for Si (silicon) during serial batch extraction.

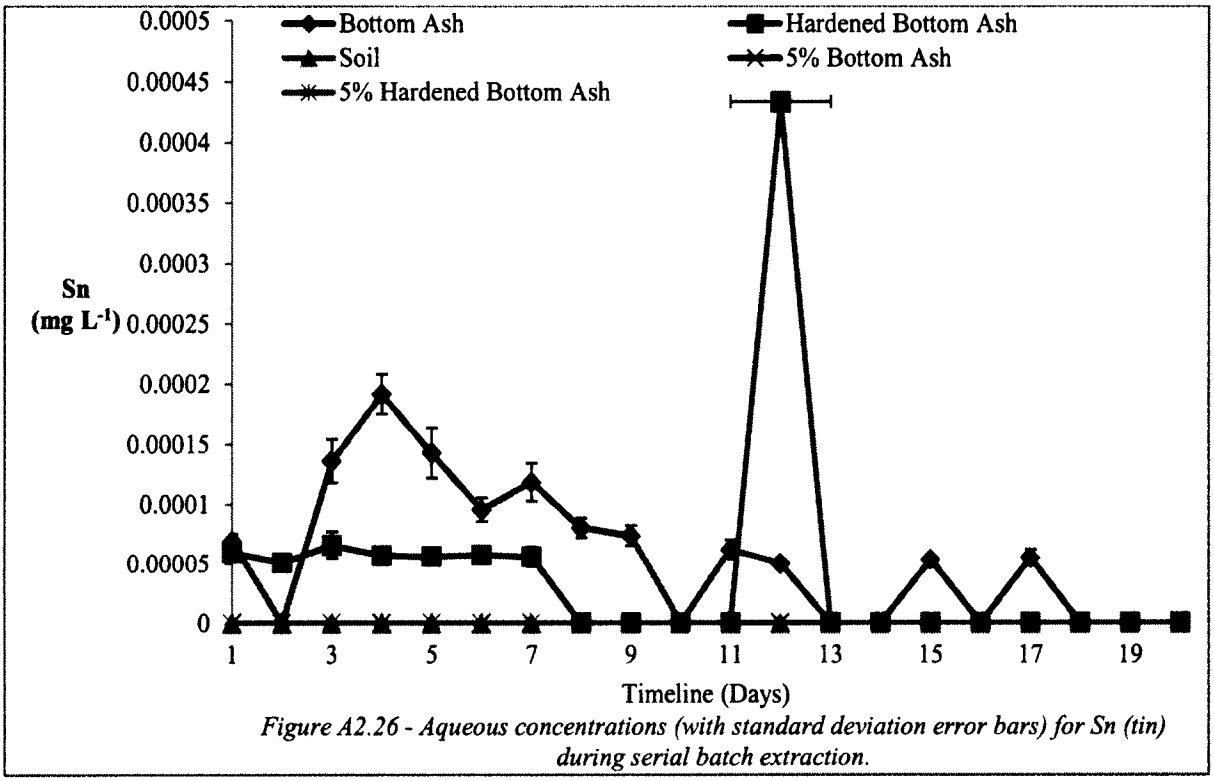

Figure A2.26 - Aqueous concentrations (with standard deviation error bars) for Sn (tin) during serial batch extraction.

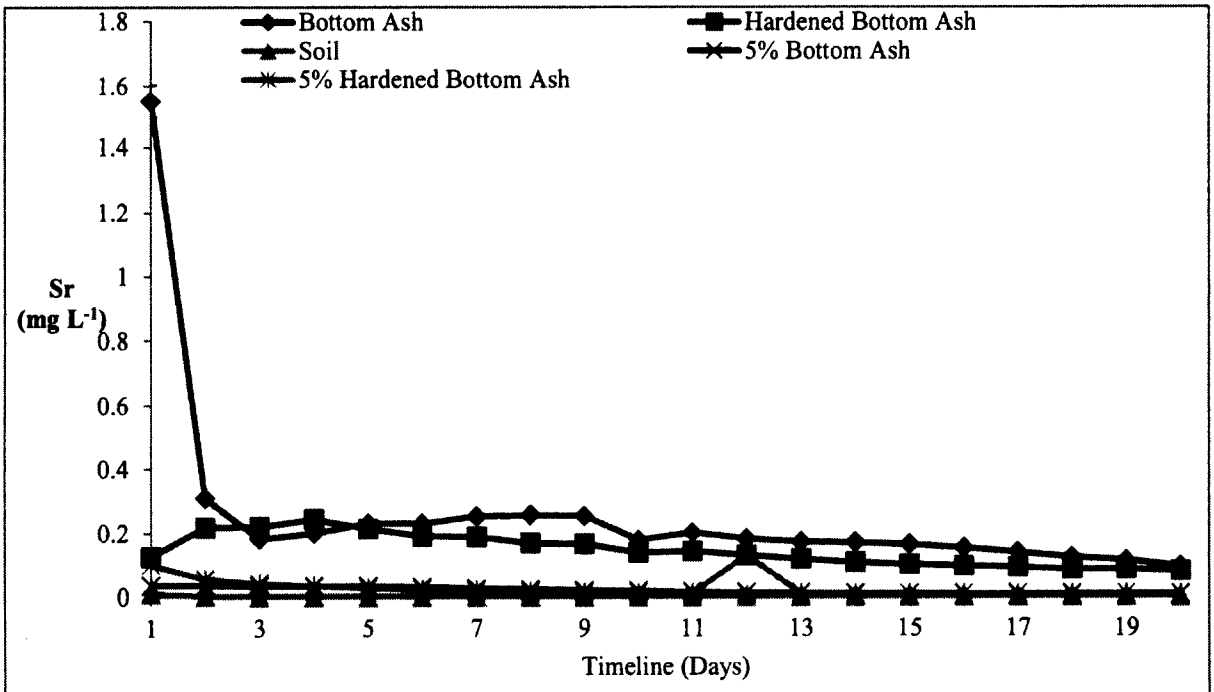

Figure A2.27 - Aqueous concentrations (with standard deviation error bars) for Sr (strontium) during serial batch extraction.

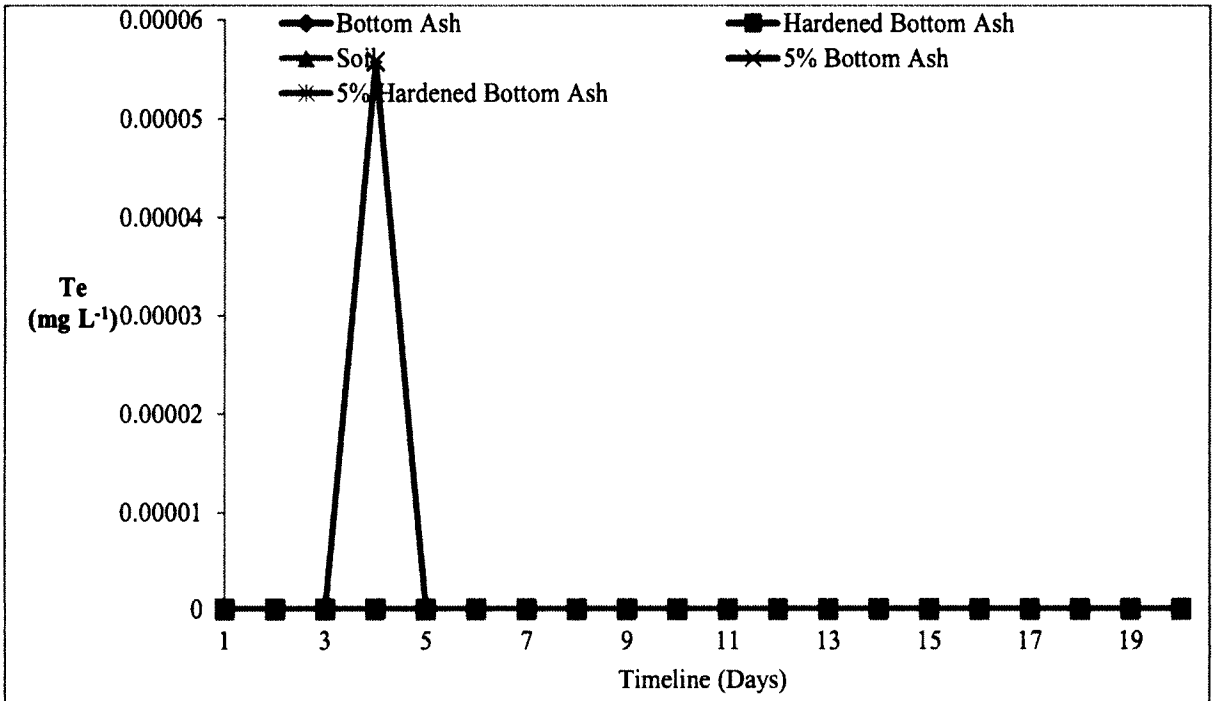

Figure A2.28 - Aqueous concentrations (with standard deviation error bars) for Te (tellurium) during serial batch extraction.

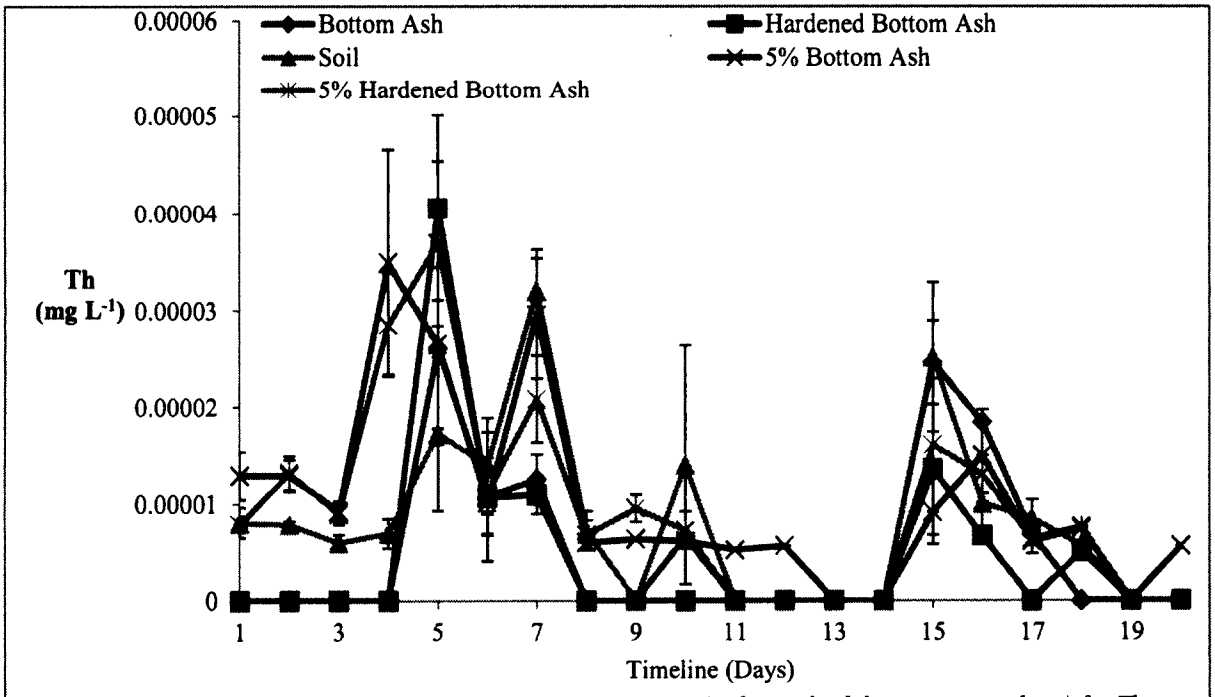

Figure A2.29 - Aqueous concentrations (with standard deviation error bars) for Th (thorium) during serial batch extraction.

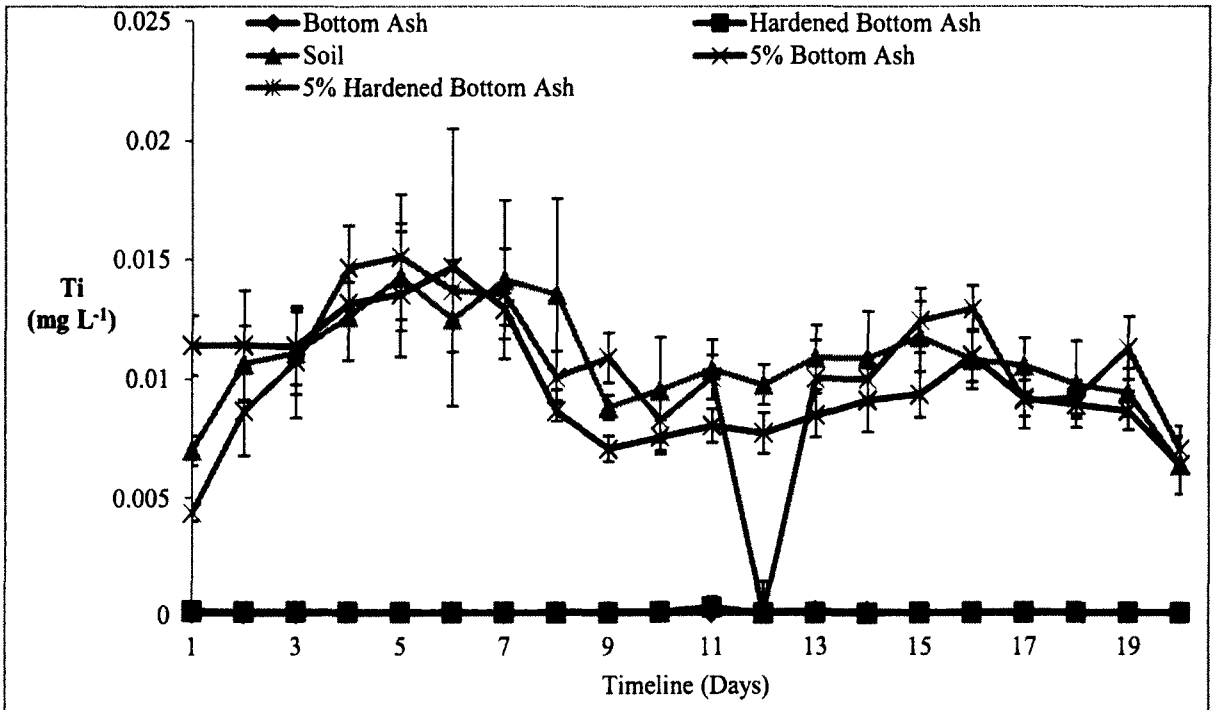

Figure A2.30 - Aqueous concentrations (with standard deviation error bars) for Ti (titanium) during serial batch extraction.

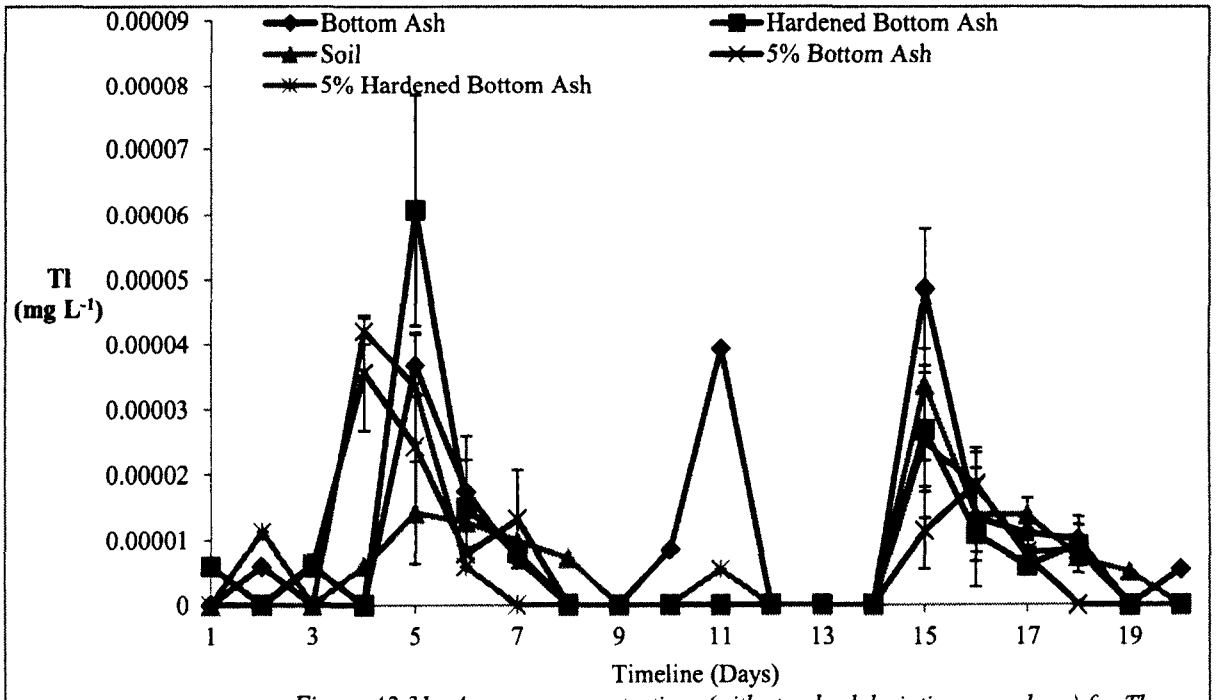

Figure A2.31 - Aqueous concentrations (with standard deviation error bars) for Tl (tantalum) during serial batch extraction.

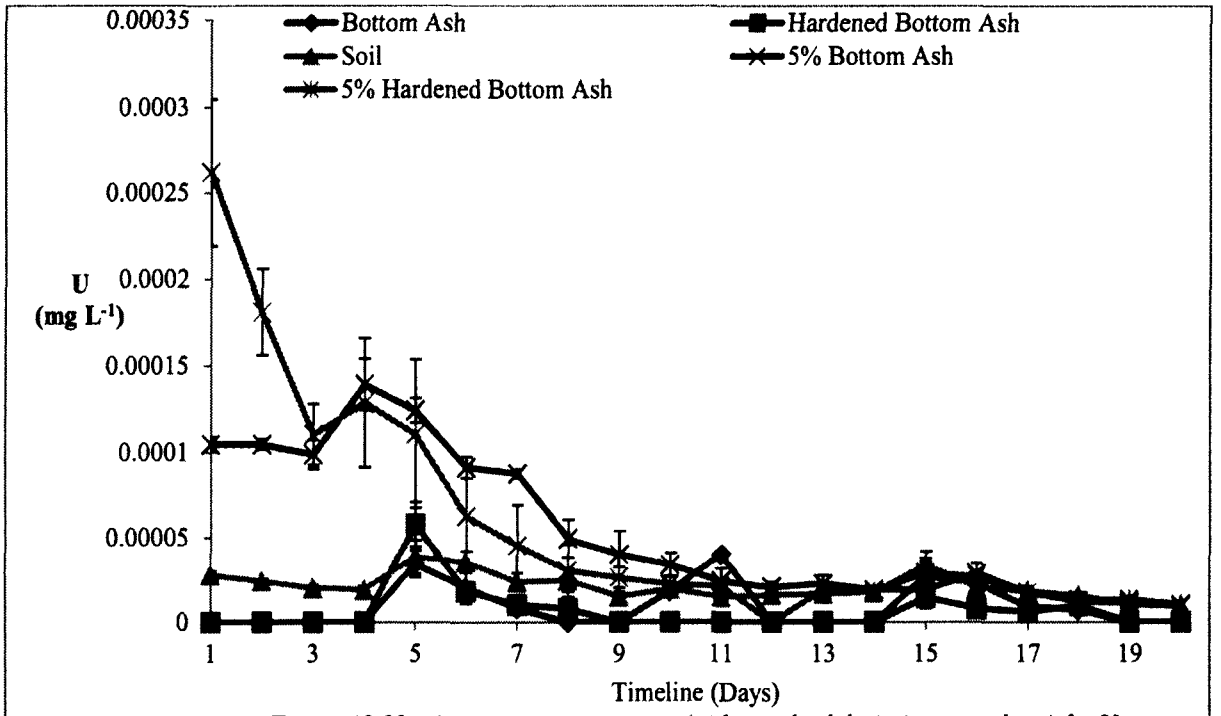

Figure A2.32 - Aqueous concentrations (with standard deviation error bars) for U (uranium) during serial batch extraction.

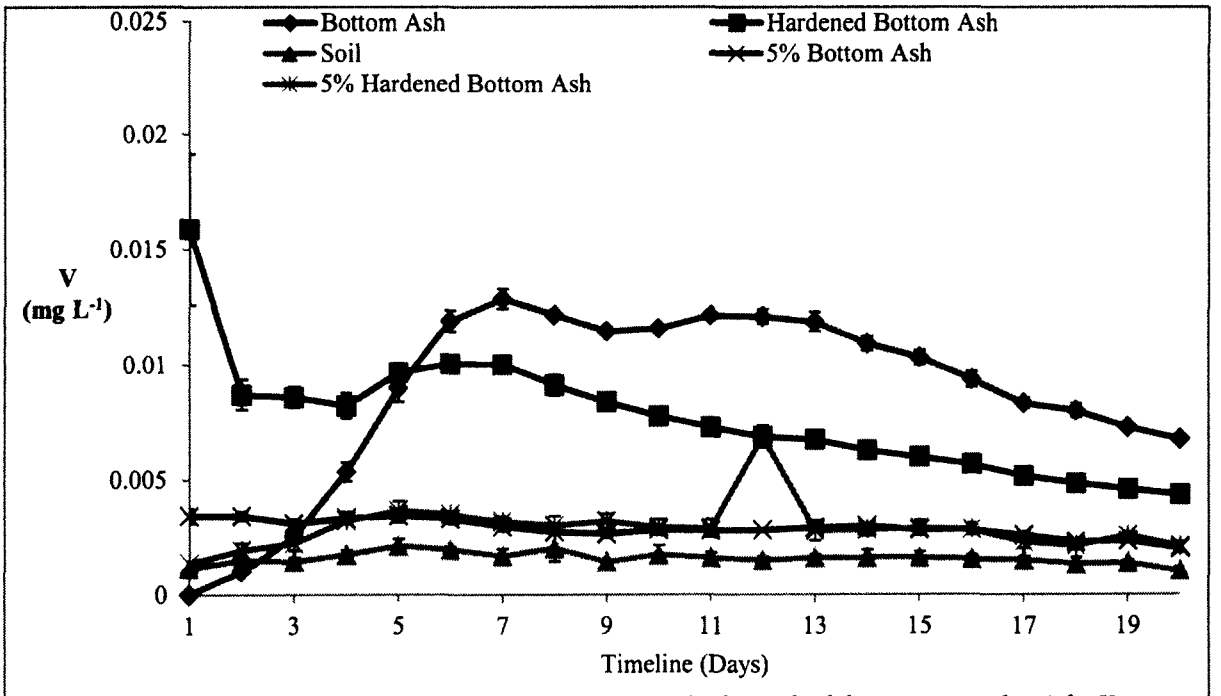

Figure A2.33 - Aqueous concentrations (with standard deviation error bars) for V (vanadium) during serial batch extraction.

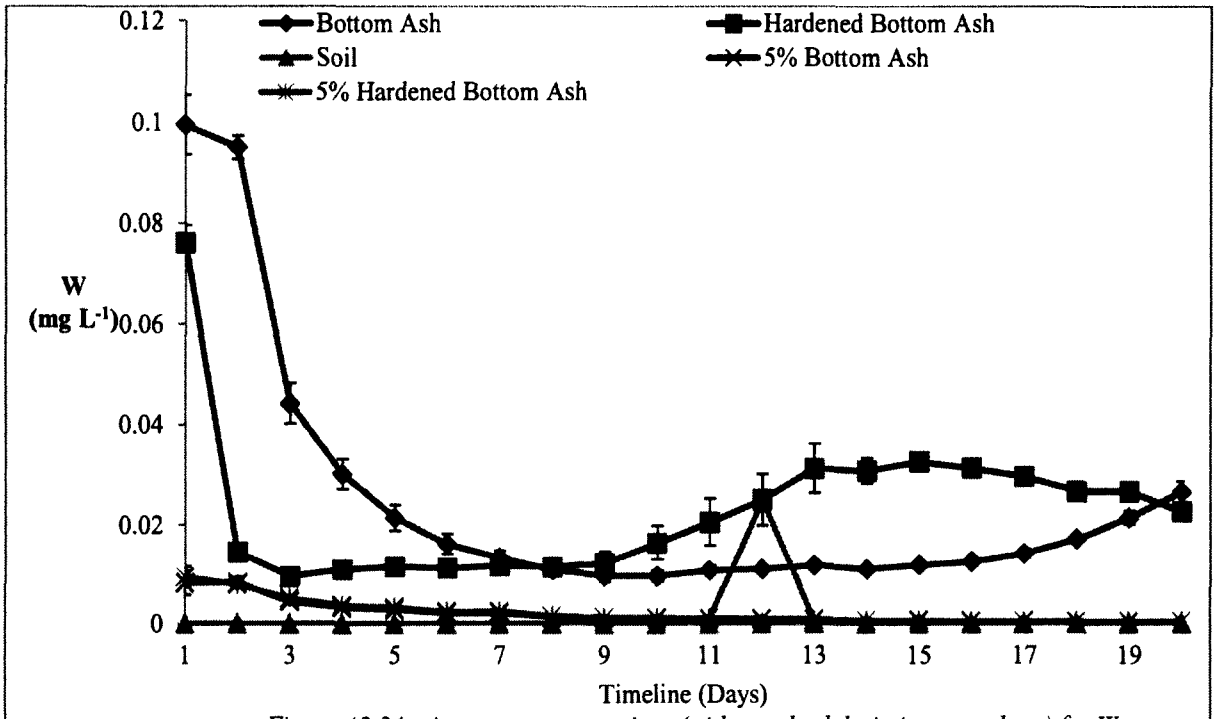

Figure A2.34 - Aqueous concentrations (with standard deviation error bars) for W (tungsten) during serial batch extraction.

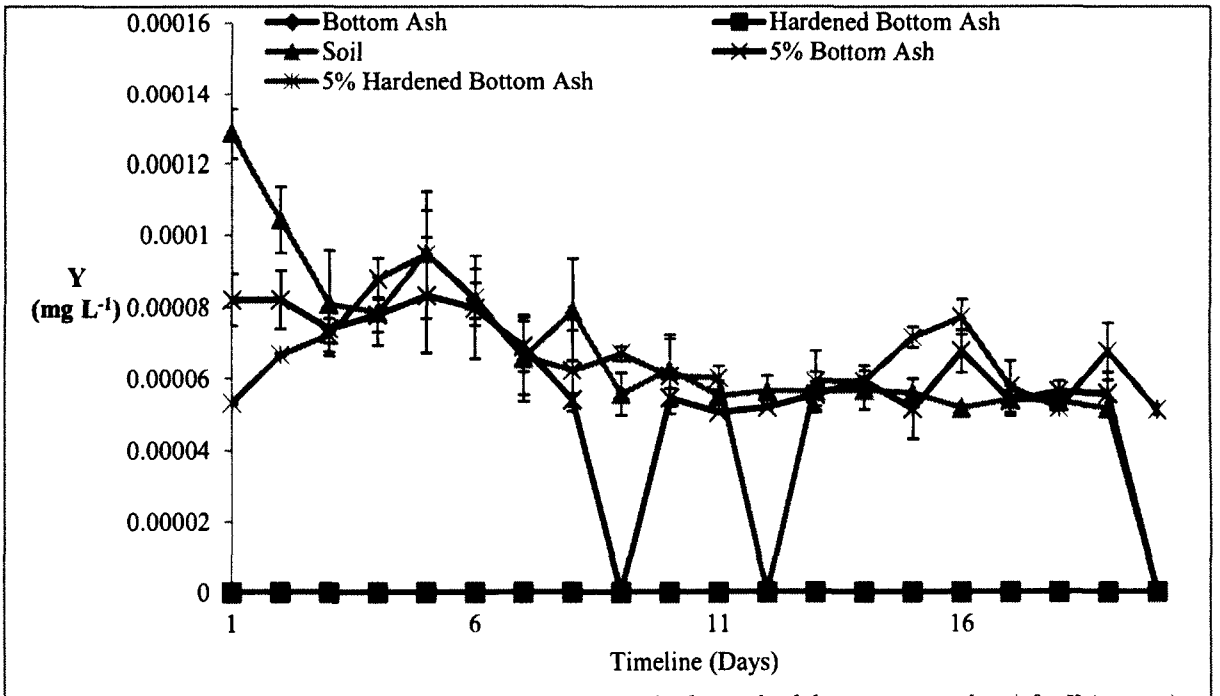

Figure A2.35 - Aqueous concentrations (with standard deviation error bars) for Y (yttrium) during serial batch extraction.

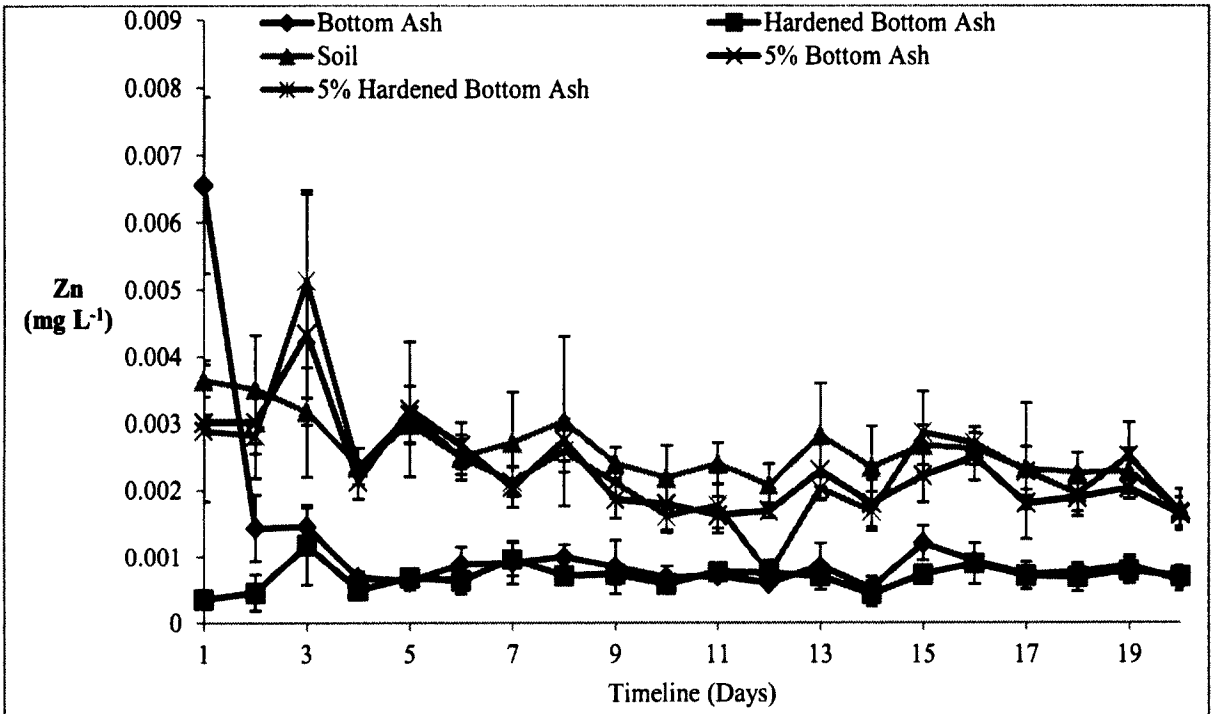

Figure A2.36 - Aqueous concentrations (with standard deviation error bars) for Zn (zinc) during serial batch extraction.

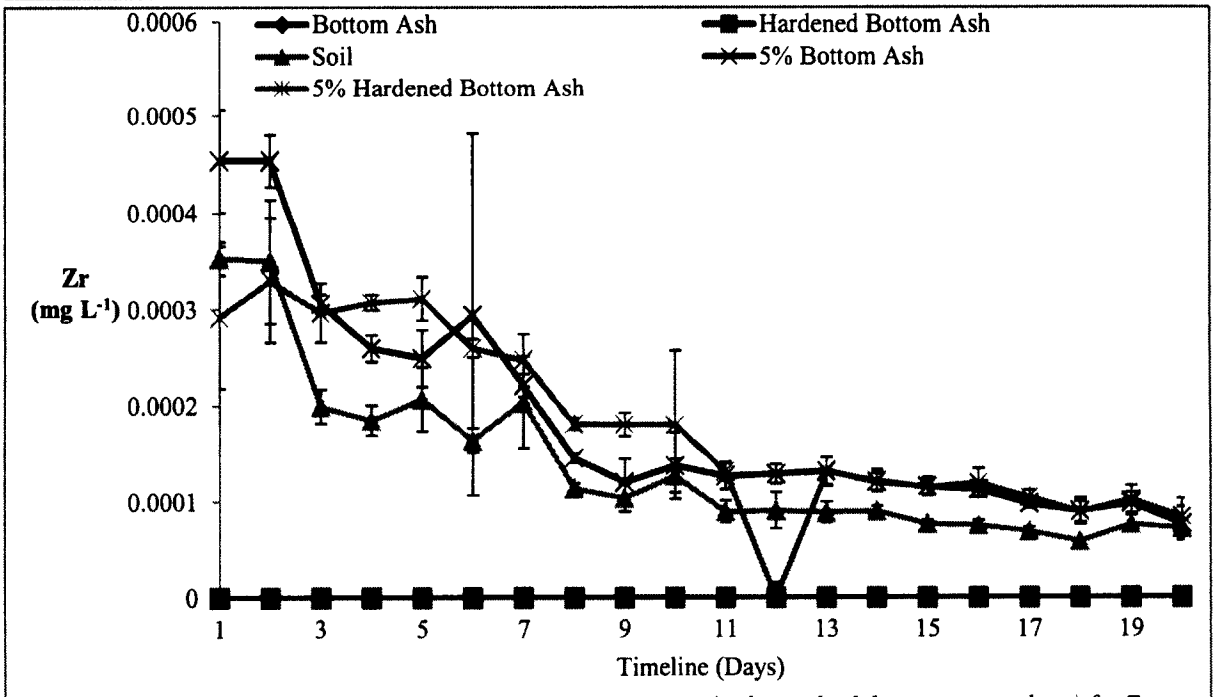

Figure A2.37 - Aqueous concentrations (with standard deviation error bars) for Zr (zirconium) during serial batch extraction.

APPENDIX A3

ANOVA Statistics Between Ash Types Using CoStat Ver. 6.3111

Analysis of Variance Table for Ag – Day One

Test: Tukey's HSD
Significance Level: 0.05
Variance: 0.28882954371
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.80999225449
MSD 0.05 = 1.17347543668

Rank	Mean Name	Mean	n	Non-significant ranges
1	SBA1	0.6265225	4	a
2	SHBA1	0.6056525	4	a
3	SOIL1	0.2125425	4	a
4	HBA1	0.1515675	4	a
5	BA1	0.0807225	4	a

Analysis of Variance Table for Ag – Day Ten

Test: Tukey's HSD
Significance Level: 0.05
Variance: 20.8732008105
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 6.8858028569
MSD 0.05 = 9.97579973099

Rank	Mean Name	Mean	n	Non-significant ranges
1	BA10	6.203	4	a
2	SHBA10	1.00925	4	a
3	SBA10	0.868125	4	a
4	HBA10	0.52265	4	a
5	SOIL10	0.36175	4	a

Analysis of Variance Table for Ag – Day Twenty

Test: Tukey's HSD
Significance Level: 0.05
Variance: 15.2876072883
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 5.89291012927
MSD 0.05 = 8.53734742397

Rank	Mean Name	Mean	n	Non-significant ranges
1	SHBA20	4.938175	4	a

2	SOIL20	0.74275	4	a
3	HBA20	0.2841	4	a
4	SBA20	0.2225	4	a
5	BA20	0.125075	4	a

Analysis of Variance Table for Al – Day One

Test: Tukey's HSD
Significance Level: 0.05
Variance: 75482.6543333
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 414.079414651
MSD 0.05 = 599.897121531

Rank	Mean Name	Mean	n	Non-significant ranges
1	HBA1	4987.25	4	a
2	SBA1	679.45	4	b
3	SOIL1	296.425	4	b
4	SHBA1	213.8	4	b
5	BA1	183.225	4	b

Analysis of Variance Table for Al – Day Ten

Test: Tukey's HSD
Significance Level: 0.05
Variance: 5579.4435
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 112.578511182
MSD 0.05 = 163.098001047

Rank	Mean Name	Mean	n	Non-significant ranges
1	HBA10	1239.5	4	a
2	BA10	1021.55	4	b
3	SBA10	629.575	4	c
4	SHBA10	513.925	4	c
5	SOIL10	235.325	4	d

Analysis of Variance Table for Al – Day Twenty

Test: Tukey's HSD
Significance Level: 0.05
Variance: 2970.17883333
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 82.1393682544
MSD 0.05 = 118.999324373

Rank	Mean Name	Mean	n	Non-significant ranges

1	BA20	1489.5	4	a
2	HBA20	666.025	4	b
3	SBA20	350.9	4	c
4	SHBA20	305.475	4	c
5	SOIL20	147.825	4	d

Analysis of Variance Table for As – Day One

Test: Tukey's HSD
Significance Level: 0.05
Variance: 0.01204918029
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.16543934813
MSD 0.05 = 0.23968008363

Rank	Mean Name	Mean	n	Non-significant ranges
1	SBA1	2.8685	4	a
2	SHBA1	1.327	4	b
3	SOIL1	0.301525	4	c
4	HBA1	0.19218	4	c
5	BA1	0.1	4	c

Analysis of Variance Table for As – Day Ten

Test: Tukey's HSD
Significance Level: 0.05
Variance: 0.00728789183
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.12866517588
MSD 0.05 = 0.18640353981

Rank	Mean Name	Mean	n	Non-significant ranges
1	SHBA10	1.04795	4	a
2	SBA10	0.945	4	a
3	BA10	0.472425	4	b
4	HBA10	0.38925	4	b
5	SOIL10	0.32275	4	b

Analysis of Variance Table for As – Day Twenty

Test: Tukey's HSD
Significance Level: 0.05
Variance: 0.00269415483
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.07822964049
MSD 0.05 = 0.11333511034

Rank	Mean Name	Mean	n	Non-significant ranges

1	SBA20	0.6668	4	a
2	BA20	0.656075	4	a
3	SHBA20	0.629725	4	a
4	HBA20	0.421275	4	b
5	SOIL20	0.2098	4	c

Analysis of Variance Table for B – Day One

Test: Tukey's HSD
Significance Level: 0.05
Variance: 1508.28393852
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 58.5331116541
MSD 0.05 = 84.7997846624

Rank	Mean Name	Mean	n	Non-significant ranges
1	HBA1	1032.9	4	a
2	SBA1	163.525	4	b
3	SHBA1	149.85	4	b
4	BA1	9.68475	4	c
5	SOIL1	6.6365	4	c

Analysis of Variance Table for B – Day Ten

Test: Tukey's HSD
Significance Level: 0.05
Variance: 93.3327421745
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 14.5605262567
MSD 0.05 = 21.0945472784

Rank	Mean Name	Mean	n	Non-significant ranges
1	BA10	167.825	4	a
2	HBA10	147.225	4	a
3	SBA10	2.2055	4	b
4	SHBA10	1.80725	4	b
5	SOIL10	0.895675	4	b

Analysis of Variance Table for B – Day Twenty

Test: Tukey's HSD
Significance Level: 0.05
Variance: 9.17715836383
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 4.56577149038
MSD 0.05 = 6.61465670047

Rank	Mean Name	Mean	n	Non-significant ranges
1	BA20	84.8075	4	a
2	HBA20	30.2225	4	b
3	SBA20	2.289	4	c
4	SHBA20	1.59885	4	c
5	SOIL20	0.183125	4	c

Analysis of Variance Table for Ba – Day One

Test: Tukey's HSD
Significance Level: 0.05
Variance: 6857.74157565
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 124.810354454
MSD 0.05 = 180.818871271

Rank	Mean Name	Mean	n	Non-significant ranges
1	BA1	3491	4	a
2	HBA1	60.77	4	b
3	SHBA1	35.0975	4	b
4	SBA1	22.4925	4	b
5	SOIL1	9.56375	4	b

Analysis of Variance Table for Ba – Day Ten

Test: Tukey's HSD
Significance Level: 0.05
Variance: 122.42030785
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 16.6758044058
MSD 0.05 = 24.159054298

Rank	Mean Name	Mean	n	Non-significant ranges
1	HBA10	366.375	4	a
2	BA10	241.8	4	b
3	SBA10	7.9215	4	c
4	SHBA10	6.919	4	c
5	SOIL10	4.17125	4	c

Analysis of Variance Table for Ba – Day Twenty

Test: Tukey's HSD
Significance Level: 0.05
Variance: 72.2003056333
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 12.806474141
MSD 0.05 = 18.5533660992

Rank	Mean Name	Mean	n	Non-significant ranges
1	HBA20	399.925	4	a
2	BA20	389.675	4	a
3	SHBA20	5.7125	4	b
4	SBA20	5.46325	4	b
5	SOIL20	2.99825	4	b

Analysis of Variance Table for Be – Day One

Test: Tukey's HSD
Significance Level: 0.05
Variance: 5.8858805e-5
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.01156287363
MSD 0.05 = 0.01675170115

Rank	Mean Name	Mean	n	Non-significant ranges
1	BA1	0.1	4	a
2	HBA1	0.1	4	a
3	SOIL1	0.1	4	a
4	SHBA1	0.1	4	a
5	SBA1	0.0914225	4	a

Analysis of Variance Table for Be – Day Ten

N/A

Analysis of Variance Table for Be – Day Twenty

N/A

Analysis of Variance Table for Bi – Day One

Test: Tukey's HSD
Significance Level: 0.05
Variance: 1.63049678e-6
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.00192450938
MSD 0.05 = 0.00278813096

Rank	Mean Name	Mean	n	Non-significant ranges
1	HBA1	0.01	4	a
2	SHBA1	0.01	4	a
3	SBA1	0.01	4	a
4	SOIL1	0.0081965	4	a
5	BA1	0.00777175	4	a

Analysis of Variance Table for Bi – Day Ten

N/A

Analysis of Variance Table for Bi – Day Twenty

Test: Tukey's HSD
Significance Level: 0.05
Variance: 3.261458e-7
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 8.60728045e-4
MSD 0.05 = 0.00124697886

Rank	Mean Name	Mean	n	Non-significant ranges
1	HBA20	0.01	4	a
2	SOIL20	0.01	4	a
3	SHBA20	0.01	4	a
4	SBA20	0.01	4	a
5	BA20	0.0093615	4	a

Analysis of Variance Table for Ca – Day One

Test: Tukey's HSD
Significance Level: 0.05
Variance: 317222355.583
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 26843.6737423
MSD 0.05 = 38889.7444295

Rank	Mean Name	Mean	n	Non-significant ranges
1	BA1	502335	4	a
2	SHBA1	20075	4	b
3	HBA1	16085	4	b
4	SBA1	13337.5	4	b
5	SOIL1	1175.75	4	b

Analysis of Variance Table for Ca – Day Ten

Test: Tukey's HSD
Significance Level: 0.05
Variance: 5955377.28867
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 3678.02518824
MSD 0.05 = 5328.53516808

Rank	Mean Name	Mean	n	Non-significant ranges
1	BA10	32231.5	4	a
2	HBA10	24634	4	b
3	SBA10	4858	4	c
4	SHBA10	2918	4	c

5	SOIL10	270.35	4	c

Analysis of Variance Table for Ca – Day Twenty

Test: Tukey's HSD
Significance Level: 0.05
Variance: 276863.194667
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 793.035578519
MSD 0.05 = 1148.90947

Rank	Mean Name	Mean	n	Non-significant ranges
1	BA20	22107.5	4	a
2	HBA20	15197.5	4	b
3	SBA20	1964.5	4	c
4	SHBA20	1655.25	4	c
5	SOIL20	168.05	4	d

Analysis of Variance Table for Cd – Day One

Test: Tukey's HSD
Significance Level: 0.05
Variance: 1.11170333e-4
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.01589112017
MSD 0.05 = 0.02302224383

Rank	Mean Name	Mean	n	Non-significant ranges
1	BA1	0.0474175	4	a
2	HBA1	0.04033	4	ab
3	SOIL1	0.03269	4	ab
4	SBA1	0.0279905	4	ab
5	SHBA1	0.0237225	4	b

Analysis of Variance Table for Cd – Day Ten

Test: Tukey's HSD
Significance Level: 0.05
Variance: 5.88336075e-5
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.01156039833
MSD 0.05 = 0.01674811506

Rank	Mean Name	Mean	n	Non-significant ranges
1	SHBA10	0.019885	4	a
2	SOIL10	0.0185425	4	a
3	SBA10	0.016835	4	a

4	BA10	0.0148275	4	a
5	HBA10	0.0081125	4	a

Analysis of Variance Table for Cd – Day Twenty

Test: Tukey's HSD
Significance Level: 0.05
Variance: 2.46003389e-4
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.02363908182
MSD 0.05 = 0.03424709521

Rank	Mean Name	Mean	n	Non-significant ranges
1	HBA20	0.027115	4	a
2	SOIL20	0.01755	4	a
3	SBA20	0.01337	4	a
4	SHBA20	0.01085675	4	a
5	BA20	0.00960675	4	a

Analysis of Variance Table for Co – Day One

Test: Tukey's HSD
Significance Level: 0.05
Variance: 0.002014385
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.06764431423
MSD 0.05 = 0.09799962992

Rank	Mean Name	Mean	n	Non-significant ranges
1	SBA1	0.6219	4	a
2	SOIL1	0.454125	4	b
3	SHBA1	0.258025	4	c
4	BA1	0.1	4	d
5	HBA1	0.1	4	d

Analysis of Variance Table for Co – Day Ten

Test: Tukey's HSD
Significance Level: 0.05
Variance: 0.00487985517
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.10528427845
MSD 0.05 = 0.15253048896

Rank	Mean Name	Mean	n	Non-significant ranges
1	SOIL10	0.646475	4	a
2	SHBA10	0.4625	4	b

3	SBA10	0.432	4	b
4	BA10	0.1	4	c
5	HBA10	0.1	4	c

Analysis of Variance Table for Co – Day Twenty

Test: Tukey's HSD
Significance Level: 0.05
Variance: 0.002282275
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.07200191469
MSD 0.05 = 0.10431269906

Rank	Mean Name	Mean	n	Non-significant ranges
1	SHBA20	0.40245	4	a
2	SOIL20	0.353925	4	a
3	SBA20	0.316825	4	a
4	BA20	0.1	4	b
5	HBA20	0.1	4	b

Analysis of Variance Table for Cr – Day One

Test: Tukey's HSD
Significance Level: 0.05
Variance: 0.6367483645
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 1.20266307725
MSD 0.05 = 1.74235688298

Rank	Mean Name	Mean	n	Non-significant ranges
1	HBA1	95.8275	4	a
2	BA1	18.93	4	b
3	SBA1	9.4125	4	c
4	SHBA1	8.507	4	c
5	SOIL1	0.532625	4	d

Analysis of Variance Table for Cr – Day Ten

Test: Tukey's HSD
Significance Level: 0.05
Variance: 0.00808707167
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.13553632469
MSD 0.05 = 0.19635810951

Rank	Mean Name	Mean	n	Non-significant ranges
1	HBA10	4.46975	4	a

2	BA10	3.47975	4	b
3	SHBA10	0.5633	4	c
4	SBA10	0.553325	4	c
5	SOIL10	0.417525	4	c

Analysis of Variance Table for Cr – Day Twenty

Test: Tukey's HSD
Significance Level: 0.05
Variance: 0.00599537033
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.11669925034
MSD 0.05 = 0.16906791762

Rank	Mean Name	Mean	n	Non-significant ranges
1	BA20	4.165	4	a
2	HBA20	4.0745	4	a
3	SHBA20	0.429125	4	b
4	SBA20	0.4052	4	b
5	SOIL20	0.311475	4	b

Analysis of Variance Table for Cu – Day One

Test: Tukey's HSD
Significance Level: 0.05
Variance: 5543.52919716
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 112.215598093
MSD 0.05 = 162.572231086

Rank	Mean Name	Mean	n	Non-significant ranges
1	BA1	92.419375	4	a
2	SBA1	6.46475	4	a
3	SHBA1	2.42875	4	a
4	SOIL1	1.1992	4	a
5	HBA1	0.3397	4	a

Analysis of Variance Table for Cu – Day Ten

Test: Tukey's HSD
Significance Level: 0.05
Variance: 0.00842361183
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.13832772421
MSD 0.05 = 0.20040214665

Rank	Mean Name	Mean	n	Non-significant ranges

1	SBA10	1.00785	4	a
2	SHBA10	0.902125	4	a
3	SOIL10	0.50625	4	b
4	BA10	0.4209	4	b
5	HBA10	0.21305	4	c

Analysis of Variance Table for Cu – Day Twenty

Test: Tukey's HSD
Significance Level: 0.05
Variance: 0.00762651833
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.13162040361
MSD 0.05 = 0.1906849229

Rank	Mean Name	Mean	n	Non-significant ranges
1	SBA20	0.60825	4	a
2	SHBA20	0.489225	4	a
3	SOIL20	0.25015	4	b
4	BA20	0.124025	4	b
5	HBA20	0.1088	4	b

Analysis of Variance Table for Fe – Day One

Test: Tukey's HSD
Significance Level: 0.05
Variance: 1101.27818319
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 50.0159562872
MSD 0.05 = 72.4605646785

Rank	Mean Name	Mean	n	Non-significant ranges
1	SOIL1	465.7	4	a
2	SBA1	415.575	4	a
3	SHBA1	182.2	4	b
4	BA1	4.489	4	c
5	HBA1	0.9023	4	c

Analysis of Variance Table for Fe – Day Ten

Test: Tukey's HSD
Significance Level: 0.05
Variance: 6608.09258095
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 122.517497751
MSD 0.05 = 177.497097508

Rank	Mean Name	Mean	n	Non-significant ranges

Rank	Mean Name	Mean	n	Non-significant ranges
1	SOIL10	616.15	4	a
2	SHBA10	431.95	4	b
3	SBA10	390.4	4	b
4	HBA10	1.2915	4	c
5	BA10	1.0161	4	c

Analysis of Variance Table for Fe – Day Twenty

Test: Tukey's HSD
Significance Level: 0.05
Variance: 1708.03888787
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 62.2886525335
MSD 0.05 = 90.2406206075

Rank	Mean Name	Mean	n	Non-significant ranges
1	SHBA20	398.3	4	a
2	SOIL20	394.075	4	a
3	SBA20	326.125	4	a
4	BA20	2.11825	4	b
5	HBA20	1.06405	4	b

Analysis of Variance Table for Hg – Day One

Test: Tukey's HSD
Significance Level: 0.05
Variance: 0.00894083926
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.14251126745
MSD 0.05 = 0.20646305058

Rank	Mean Name	Mean	n	Non-significant ranges
1	BA1	2.307	4	a
2	HBA1	1.5205	4	b
3	SBA1	0.411425	4	c
4	SHBA1	0.1651575	4	d
5	SOIL1	0.01	4	d

Analysis of Variance Table for Hg – Day Ten

Test: Tukey's HSD
Significance Level: 0.05
Variance: 0.0018053241
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.0640379836
MSD 0.05 = 0.09277496217

Rank	Mean Name	Mean	n	Non-significant ranges
1	HBA10	0.341975	4	a
2	BA10	0.188425	4	b
3	SHBA10	0.01087	4	c
4	SOIL10	0.01	4	c
5	SBA10	0.0090175	4	c

Analysis of Variance Table for Hg – Day Twenty

Test: Tukey's HSD
Significance Level: 0.05
Variance: 0.00120661167
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.05235327072
MSD 0.05 = 0.07584674653

Rank	Mean Name	Mean	n	Non-significant ranges
1	BA20	0.496375	4	a
2	HBA20	0.416775	4	b
3	SOIL20	0.01	4	c
4	SHBA20	0.01	4	c
5	SBA20	0.01	4	c

Analysis of Variance Table for K – Day One

Test: Tukey's HSD
Significance Level: 0.05
Variance: 6229973.00796
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 3761.86443886
MSD 0.05 = 5449.99719526

Rank	Mean Name	Mean	n	Non-significant ranges
1	HBA1	121655.1	4	a
2	BA1	101942.6	4	b
3	SHBA1	4821.4875	4	c
4	SBA1	3665.1	4	c
5	SOIL1	1001.775	4	c

Analysis of Variance Table for K – Day Ten

Test: Tukey's HSD
Significance Level: 0.05
Variance: 10885.8376667
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 157.250120077
MSD 0.05 = 227.815947996

Rank	Mean Name	Mean	n	Non-significant ranges
1	BA10	5039	4	a
2	HBA10	4781.75	4	b
3	SHBA10	532.025	4	c
4	SBA10	471.475	4	c
5	SOIL10	230.1	4	d

Analysis of Variance Table for K – Day Twenty

Test: Tukey's HSD
Significance Level: 0.05
Variance: 9254.56275792
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 144.989987137
MSD 0.05 = 210.054093145

Rank	Mean Name	Mean	n	Non-significant ranges
1	HBA20	3774.1125	4	a
2	BA20	3367.0375	4	b
3	SHBA20	334.1625	4	c
4	SBA20	304.11875	4	cd
5	SOIL20	115.1875	4	d

Analysis of Variance Table for Li – Day One

Test: Tukey's HSD
Significance Level: 0.05
Variance: 0.00708396938
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.12685231476
MSD 0.05 = 0.18377715915

Rank	Mean Name	Mean	n	Non-significant ranges
1	BA1	2.3505	4	a
2	HBA1	1.43325	4	b
3	SHBA1	0.1	4	c
4	SBA1	0.1	4	c
5	SOIL1	0.0951325	4	c

Analysis of Variance Table for Li – Day Ten

Test: Tukey's HSD
Significance Level: 0.05
Variance: 0.00231544983
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.07252333164

MSD 0.05 = 0.10506810133

Rank	Mean Name	Mean	n	Non-significant ranges
1	HBA10	0.447575	4	a
2	BA10	0.217	4	b
3	SOIL10	0.1	4	c
4	SHBA10	0.1	4	c
5	SBA10	0.1	4	c

Analysis of Variance Table for Li – Day Twenty

Test: Tukey's HSD
Significance Level: 0.05
Variance: 0.00521787924
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.10886971115
MSD 0.05 = 0.15772488085

Rank	Mean Name	Mean	n	Non-significant ranges
1	HBA20	0.829375	4	a
2	BA20	0.45435	4	b
3	SOIL20	0.1651325	4	c
4	SBA20	0.148225	4	c
5	SHBA20	0.0848075	4	c

Analysis of Variance Table for Mg – Day One

Test: Tukey's HSD
Significance Level: 0.05
Variance: 12728.5950117
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 170.039685579
MSD 0.05 = 246.344817722

Rank	Mean Name	Mean	n	Non-significant ranges
1	SHBA1	6143.75	4	a
2	SBA1	2887.75	4	b
3	SOIL1	753.325	4	c
4	BA1	34.8425	4	d
5	HBA1	17.31	4	d

Analysis of Variance Table for Mg – Day Ten

Test: Tukey's HSD
Significance Level: 0.05
Variance: 1302.42116667
Degrees of Freedom: 15
Keep If:

n Means = 5

LSD 0.05 = 54.3920943789
MSD 0.05 = 78.8004901897

Rank	Mean Name	Mean	n	Non-significant ranges
1	SBA10	458.425	4	a
2	SHBA10	355.075	4	b
3	HBA10	192.125	4	c
4	SOIL10	151.075	4	c
5	BA10	130.425	4	c

Analysis of Variance Table for Mg – Day Twenty
Test: Tukey's HSD
Significance Level: 0.05
Variance: 1231.03316667
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 52.8804248714
MSD 0.05 = 76.6104605622

Rank	Mean Name	Mean	n	Non-significant ranges
1	HBA20	598.65	4	a
2	BA20	348.225	4	b
3	SHBA20	249.85	4	c
4	SBA20	234.25	4	c
5	SOIL20	125.2	4	d

Analysis of Variance Table for Mn – Day One
Test: Tukey's HSD
Significance Level: 0.05
Variance: 22.0142052023
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 7.07150029931
MSD 0.05 = 10.2448287076

Rank	Mean Name	Mean	n	Non-significant ranges
1	SBA1	50.1125	4	a
2	SOIL1	38.2875	4	b
3	SHBA1	23.2675	4	c
4	BA1	0.356475	4	d
5	HBA1	0.143475	4	d

Analysis of Variance Table for Mn – Day Ten
Test: Tukey's HSD
Significance Level: 0.05
Variance: 58.2584875825
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 11.5037560088
MSD 0.05 = 16.6660545593

Rank	Mean Name	Mean	n	Non-significant ranges
1	SOIL10	63.9375	4	a
2	SHBA10	59.3925	4	a
3	SBA10	59.1825	4	a
4	HBA10	0.438025	4	b
5	BA10	0.30815	4	b

Analysis of Variance Table for Mn – Day Twenty
Test: Tukey's HSD
Significance Level: 0.05
Variance: 23.552555057
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 7.31440616397
MSD 0.05 = 10.5967383266

Rank	Mean Name	Mean	n	Non-significant ranges
1	SHBA20	48.3075	4	a
2	SBA20	42.5575	4	ab
3	SOIL20	35.3275	4	b
4	BA20	0.877625	4	c
5	HBA20	0.430575	4	c

Analysis of Variance Table for Mo – Day One
Test: Tukey's HSD
Significance Level: 0.05
Variance: 4.49338302733
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 3.19482282969
MSD 0.05 = 4.62849625343

Rank	Mean Name	Mean	n	Non-significant ranges
1	HBA1	71.38	4	a
2	BA1	63.44	4	b
3	SBA1	8.9725	4	c
4	SHBA1	7.3025	4	c
5	SOIL1	0.23945	4	d

Analysis of Variance Table for Mo – Day Ten
Test: Tukey's HSD
Significance Level: 0.05
Variance: 0.00202547238
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.06783021934
MSD 0.05 = 0.09826895975

Rank	Mean Name	Mean	n	Non-significant ranges
1	HBA10	1.9505	4	a
2	BA10	1.4105	4	b
3	SBA10	0.338425	4	c
4	SHBA10	0.270025	4	c
5	SOIL10	0.1012125	4	d

Analysis of Variance Table for Mo – Day Twenty
Test: Tukey's HSD
Significance Level: 0.05
Variance: 0.00616703509
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.11835817739
MSD 0.05 = 0.17147128646

Rank	Mean Name	Mean	n	Non-significant ranges
1	HBA20	2.448	4	a
2	BA20	1.6035	4	b
3	SBA20	0.1651	4	c
4	SHBA20	0.150375	4	c
5	SOIL20	0.071965	4	c

Analysis of Variance Table for Na – Day One
Test: Tukey's HSD
Significance Level: 0.05
Variance: 51045.16
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 340.515859244
MSD 0.05 = 493.321997106

Rank	Mean Name	Mean	n	Non-significant ranges
1	HBA1	13260	4	a
2	BA1	8668.75	4	b
3	SHBA1	1677.5	4	c
4	SBA1	1482	4	c
5	SOIL1	451.65	4	d

Analysis of Variance Table for Na – Day Ten
Test: Tukey's HSD
Significance Level: 0.05
Variance: 4999.75939833
Degrees of Freedom: 15

Keep If:

n Means = 5
LSD 0.05 = 106.569913096
MSD 0.05 = 154.393050815

Rank	Mean Name	Mean	n	Non-significant ranges
1	BA10	1051.95	4	a
2	HBA10	1017.85	4	a
3	SOIL10	115.925	4	b
4	SHBA10	103.1175	4	b
5	SBA10	83.13	4	b

Analysis of Variance Table for Na – Day Twenty
Test: Tukey's HSD
Significance Level: 0.05
Variance: 106.297871667
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 15.5389741213
MSD 0.05 = 22.5120726051

Rank	Mean Name	Mean	n	Non-significant ranges
1	BA20	679.975	4	a
2	HBA20	647.375	4	b
3	SHBA20	87.84	4	c
4	SBA20	87.7375	4	c
5	SOIL20	35.29	4	d

Analysis of Variance Table for Ni – Day One
Test: Tukey's HSD
Significance Level: 0.05
Variance: 0.0528988789
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.34664368507
MSD 0.05 = 0.5021996784

Rank	Mean Name	Mean	n	Non-significant ranges
1	SBA1	2.4345	4	a
2	SHBA1	1.31295	4	b
3	SOIL1	0.835975	4	b
4	BA1	0.28325	4	c
5	HBA1	0.06498	4	c

Analysis of Variance Table for Ni – Day Ten
Test: Tukey's HSD
Significance Level: 0.05
Variance: 0.00311153026

Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.08407116648
MSD 0.05 = 0.12179801504

Rank	Mean Name	Mean	n	Non-significant ranges
1	SBA10	0.437775	4	a
2	SOIL10	0.360775	4	a
3	SHBA10	0.349525	4	a
4	BA10	0.1157475	4	b
5	HBA10	0.088195	4	b

Analysis of Variance Table for Ni – Day Twenty
Test: Tukey's HSD
Significance Level: 0.05
Variance: 0.00327378808
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.086235352
MSD 0.05 = 0.12493337657

Rank	Mean Name	Mean	n	Non-significant ranges
1	SBA20	0.276925	4	a
2	SHBA20	0.273925	4	a
3	SOIL20	0.236625	4	ab
4	BA20	0.147515	4	bc
5	HBA20	0.1	4	c

Analysis of Variance Table for P – Day One
Test: Tukey's HSD
Significance Level: 0.05
Variance: 341.4508428
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 27.8499329172
MSD 0.05 = 40.3475613632

Rank	Mean Name	Mean	n	Non-significant ranges
1	SBA1	368.95	4	a
2	SHBA1	148.675	4	b
3	HBA1	74.8675	4	c
4	SOIL1	61.23	4	c
5	BA1	0.3335	4	d

Analysis of Variance Table for P – Day Ten
Test: Tukey's HSD
Significance Level: 0.05

Variance: 3557.03804333
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 89.8885373967
MSD 0.05 = 130.225925112

Rank	Mean Name	Mean	n	Non-significant ranges
1	SHBA10	293.9	4	a
2	SBA10	242.175	4	ab
3	SOIL10	118.1325	4	bc
4	BA10	105.8	4	c
5	HBA10	63.6375	4	c

Analysis of Variance Table for P – Day Twenty
Test: Tukey's HSD
Significance Level: 0.05
Variance: 259.38515
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 24.2735118182
MSD 0.05 = 35.1662250137

Rank	Mean Name	Mean	n	Non-significant ranges
1	SHBA20	184.45	4	a
2	SBA20	171.225	4	a
3	SOIL20	37.1325	4	b
4	BA20	36.86	4	b
5	HBA20	34.9875	4	b

Analysis of Variance Table for Pb – Day One
Test: Tukey's HSD
Significance Level: 0.05
Variance: 0.01757667902
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.199815176
MSD 0.05 = 0.28948202852

Rank	Mean Name	Mean	n	Non-significant ranges
1	BA1	1.30316675	4	a
2	SOIL1	0.28393325	4	b
3	SBA1	0.24551675	4	b
4	SHBA1	0.12688675	4	b
5	HBA1	0.03109	4	b

Analysis of Variance Table for Pb – Day Ten
Test: Tukey's HSD

Significance Level: 0.05
Variance: 0.0194144822
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.21000177472
MSD 0.05 = 0.30423985283

Rank	Mean Name	Mean	n	Non-significant ranges
1	SOIL10	0.3551	4	a
2	SHBA10	0.23368333333	4	ab
3	SBA10	0.22135833333	4	ab
4	BA10	0.19131666667	4	ab
5	HBA10	0.04638333333	4	b

Analysis of Variance Table for Pb – Day Twenty
Test: Tukey's HSD
Significance Level: 0.05
Variance: 0.11413857271
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.50918579288
MSD 0.05 = 0.73768238813

Rank	Mean Name	Mean	n	Non-significant ranges
1	HBA20	0.3972625	4	a
2	SOIL20	0.3167415	4	a
3	SBA20	0.27156675	4	a
4	SHBA20	0.27083325	4	a
5	BA20	0.05700825	4	a

Analysis of Variance Table for Sb – Day One
Test: Tukey's HSD
Significance Level: 0.05
Variance: 0.03505279641
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.28217685849
MSD 0.05 = 0.40880343041

Rank	Mean Name	Mean	n	Non-significant ranges
1	HBA1	4.425	4	a
2	SBA1	1.3815	4	b
3	SHBA1	1.351	4	b
4	BA1	0.49305	4	c
5	SOIL1	0.027785	4	d

Analysis of Variance Table for Sb – Day Ten

Test: Tukey's HSD
Significance Level: 0.05
Variance: 7.75841938e-4
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.04198041087
MSD 0.05 = 0.06081907661

Rank	Mean Name	Mean	n	Non-significant ranges
1	HBA10	0.84575	4	a
2	BA10	0.693875	4	b
3	SBA10	0.15155	4	c
4	SHBA10	0.108615	4	c
5	SOIL10	0.0133275	4	d

Analysis of Variance Table for Sb – Day Twenty

Test: Tukey's HSD
Significance Level: 0.05
Variance: 5.64556738e-4
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.03581078627
MSD 0.05 = 0.05188083938

Rank	Mean Name	Mean	n	Non-significant ranges
1	HBA20	1.08025	4	a
2	BA20	0.898025	4	b
3	SBA20	0.0442975	4	c
4	SHBA20	0.04177	4	c
5	SOIL20	0.01088775	4	c

Analysis of Variance Table for Se – Day One

Test: Tukey's HSD
Significance Level: 0.05
Variance: 0.0039749445
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.09502231209
MSD 0.05 = 0.13766347587

Rank	Mean Name	Mean	n	Non-significant ranges
1	HBA1	0.96985	4	a
2	BA1	0.400825	4	b
3	SBA1	0.29545	4	b
4	SHBA1	0.1108	4	c

5	SOIL1	0.1	4	c

Analysis of Variance Table for Se – Day Ten

Test: Tukey's HSD
Significance Level: 0.05
Variance: 0.00105478353
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.04894876387
MSD 0.05 = 0.07091447078

Rank	Mean Name	Mean	n	Non-significant ranges
1	SHBA10	0.130715	4	a
2	SOIL10	0.0962575	4	a
3	BA10	0.09214	4	a
4	HBA10	0.088965	4	a
5	SBA10	0.0821425	4	a

Analysis of Variance Table for Se – Day Twenty

N/A

Analysis of Variance Table for Si – Day One

Test: Tukey's HSD
Significance Level: 0.05
Variance: 536712.246
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 1104.15695196
MSD 0.05 = 1599.64623636

Rank	Mean Name	Mean	n	Non-significant ranges
1	HBA1	11338.75	4	a
2	SHBA1	3165.75	4	b
3	SBA1	2469.75	4	bc
4	SOIL1	1103.25	4	cd
5	BA1	283.75	4	d

Analysis of Variance Table for Si – Day Ten

Test: Tukey's HSD
Significance Level: 0.05
Variance: 86987.421
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 444.516909696
MSD 0.05 = 643.993410837

Rank	Mean Name	Mean	n	Non-significant ranges

1	BA10	15987.5	4	a
2	HBA10	10311.5	4	b
3	SHBA10	1224	4	c
4	SBA10	966.175	4	cd
5	SOIL10	328.175	4	d

Analysis of Variance Table for Si – Day Twenty

Test: Tukey's HSD
Significance Level: 0.05
Variance: 27127.6106667
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 248.236609476
MSD 0.05 = 359.632529931

Rank	Mean Name	Mean	n	Non-significant ranges
1	BA20	6312.75	4	a
2	HBA20	5365.75	4	b
3	SHBA20	996.6	4	c
4	SBA20	863.6	4	c
5	SOIL20	231.1	4	d

Analysis of Variance Table for Sn – Day One

Test: Tukey's HSD
Significance Level: 0.05
Variance: 1.49117372e-4
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.0184045066
MSD 0.05 = 0.0266635098

Rank	Mean Name	Mean	n	Non-significant ranges
1	SOIL1	0.1	4	a
2	SHBA1	0.1	4	a
3	SBA1	0.1	4	a
4	BA1	0.084635	4	ab
5	HBA1	0.0698575	4	b

Analysis of Variance Table for Sn – Day Ten

N/A

Analysis of Variance Table for Sn – Day Twenty

N/A

Analysis of Variance Table for Sr – Day One

Test: Tukey's HSD
Significance Level: 0.05
Variance: 388.313575
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 29.6996509706
MSD 0.05 = 43.0273384702

Rank	Mean Name	Mean	n	Non-significant ranges
1	BA1	1566.75	4	a
2	HBA1	127.2	4	b
3	SHBA1	101.9875	4	bc
4	SBA1	59.1325	4	c
5	SOIL1	10.9625	4	d

Analysis of Variance Table for Sr – Day Ten
Test: Tukey's HSD
Significance Level: 0.05
Variance: 27.0283649167
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 7.83555829113
MSD 0.05 = 11.351756929

Rank	Mean Name	Mean	n	Non-significant ranges
1	BA10	179.4	4	a
2	HBA10	139.175	4	b
3	SBA10	16.665	4	c
4	SHBA10	10.5685	4	cd
5	SOIL10	1.97125	4	d

Analysis of Variance Table for Sr – Day Twenty
Test: Tukey's HSD
Significance Level: 0.05
Variance: 3.66521691667
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 2.88542572941
MSD 0.05 = 4.18025752602

Rank	Mean Name	Mean	n	Non-significant ranges
1	BA20	94.015	4	a
2	HBA20	79.1225	4	b
3	SBA20	7.5565	4	c
4	SHBA20	6.8335	4	c
5	SOIL20	1.66975	4	d

Analysis of Variance Table for Te – Day One
N/A

Analysis of Variance Table for Te – Day Ten
N/A

Analysis of Variance Table for Te – Day Twenty
N/A

Analysis of Variance Table for Th – Day One
Test: Tukey's HSD
Significance Level: 0.05
Variance: 1.84826932e-6
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.00204900343
MSD 0.05 = 0.00296849159

Rank	Mean Name	Mean	n	Non-significant ranges
1	SBA1	0.0168475	4	a
2	BA1	0.01	4	b
3	HBA1	0.01	4	b
4	SOIL1	0.008106	4	b
5	SHBA1	0.00795275	4	b

Analysis of Variance Table for Th – Day Ten
Test: Tukey's HSD
Significance Level: 0.05
Variance: 1.345354e-5
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.00552813125
MSD 0.05 = 0.0080088744

Rank	Mean Name	Mean	n	Non-significant ranges
1	SOIL10	0.0120115	4	a
2	HBA10	0.01	4	a
3	BA10	0.00915775	4	a
4	SBA10	0.0090465	4	a
5	SHBA10	0.00800825	4	a

Analysis of Variance Table for Th – Day Twenty
Test: Tukey's HSD
Significance Level: 0.05
Variance: 9.4656005e-7
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.00146633819
MSD 0.05 = 0.00212435592

Rank	Mean Name	Mean	n	Non-significant ranges
1	BA20	0.01	4	a

2	HBA20	0.01	4	a
3	SOIL20	0.01	4	a
4	SHBA20	0.01	4	a
5	SBA20	0.00891225	4	a

Analysis of Variance Table for Ti – Day One

Test: Tukey's HSD
Significance Level: 0.05
Variance: 0.41977617335
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.9764925877
MSD 0.05 = 1.41469262135

Rank	Mean Name	Mean	n	Non-significant ranges
1	SBA1	9.11575	4	a
2	SOIL1	6.99325	4	b
3	SHBA1	4.3805	4	c
4	HBA1	0.1781525	4	d
5	BA1	0.10079	4	d

Analysis of Variance Table for Ti – Day Ten

Test: Tukey's HSD
Significance Level: 0.05
Variance: 1.3978179249
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 1.78190834442
MSD 0.05 = 2.58153786164

Rank	Mean Name	Mean	n	Non-significant ranges
1	SOIL10	9.54275	4	a
2	SHBA10	8.281	4	a
3	SBA10	7.57225	4	a
4	HBA10	0.13633	4	b
5	BA10	0.1149925	4	b

Analysis of Variance Table for Ti – Day Twenty

Test: Tukey's HSD
Significance Level: 0.05
Variance: 0.50706037716
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 1.07322281491
MSD 0.05 = 1.55483043746

Rank	Mean Name	Mean	n	Non-significant ranges

1	SHBA20	7.02225	4	a
2	SBA20	6.3635	4	a
3	SOIL20	6.36225	4	a
4	HBA20	0.09658	4	b
5	BA20	0.0719	4	b

Analysis of Variance Table for Tl – Day One

Test: Tukey's HSD
Significance Level: 0.05
Variance: 8.413202e-7
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.00138242226
MSD 0.05 = 0.00200278281

Rank	Mean Name	Mean	n	Non-significant ranges
1	BA1	0.01	4	a
2	SOIL1	0.01	4	a
3	SHBA1	0.01	4	a
4	SBA1	0.01	4	a
5	HBA1	0.0089745	4	a

Analysis of Variance Table for Tl – Day Ten

Test: Tukey's HSD
Significance Level: 0.05
Variance: 1.02245e-7
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 4.81926823e-4
MSD 0.05 = 6.98190983e-4

Rank	Mean Name	Mean	n	Non-significant ranges
1	HBA10	0.01	4	a
2	SOIL10	0.01	4	a
3	SHBA10	0.01	4	a
4	SBA10	0.01	4	a
5	BA10	0.0096425	4	a

Analysis of Variance Table for Tl – Day Twenty

Test: Tukey's HSD
Significance Level: 0.05
Variance: 9.9502605e-7
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.00150340948
MSD 0.05 = 0.00217806292

Rank	Mean Name	Mean	n	Non-significant ranges

Rank	Mean Name	Mean	n	Non-significant ranges
1	HBA20	0.01	4	a
2	SOIL20	0.01	4	a
3	SHBA20	0.01	4	a
4	SBA20	0.01	4	a
5	BA20	0.00888475	4	a

Analysis of Variance Table for U – Day One

Test: Tukey's HSD
Significance Level: 0.05
Variance: 3.68876758e-4
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.02894680965
MSD 0.05 = 0.04193666039

Rank	Mean Name	Mean	n	Non-significant ranges
1	SHBA1	0.26195	4	a
2	SBA1	0.150175	4	b
3	SOIL1	0.0277225	4	c
4	BA1	0.01	4	c
5	HBA1	0.01	4	c

Analysis of Variance Table for U – Day Ten

Test: Tukey's HSD
Significance Level: 0.05
Variance: 2.1445495e-5
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.00697956083
MSD 0.05 = 0.01011163149

Rank	Mean Name	Mean	n	Non-significant ranges
1	SBA10	0.0337675	4	a
2	SHBA10	0.02229	4	b
3	SOIL10	0.0194375	4	bc
4	BA10	0.0120375	4	c
5	HBA10	0.01	4	c

Analysis of Variance Table for U – Day Twenty

Test: Tukey's HSD
Significance Level: 0.05
Variance: 1.67183338e-6
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.00194875192
MSD 0.05 = 0.00282325231

Rank	Mean Name	Mean	n	Non-significant ranges
1	SHBA20	0.010308	4	a
2	BA20	0.01	4	a
3	HBA20	0.01	4	a
4	SOIL20	0.009407	4	a
5	SBA20	0.00926475	4	a

Analysis of Variance Table for V – Day One

Test: Tukey's HSD
Significance Level: 0.05
Variance: 2.15880398333
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 2.21445400505
MSD 0.05 = 3.20818793784

Rank	Mean Name	Mean	n	Non-significant ranges
1	HBA1	15.8975	4	a
2	SBA1	3.146	4	b
3	SHBA1	1.42275	4	b
4	SOIL1	1.176	4	b
5	BA1	0.1	4	b

Analysis of Variance Table for V – Day Ten

Test: Tukey's HSD
Significance Level: 0.05
Variance: 0.06817981667
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.39353917736
MSD 0.05 = 0.5701394741

Rank	Mean Name	Mean	n	Non-significant ranges
1	BA10	11.6075	4	a
2	HBA10	7.79575	4	b
3	SHBA10	2.96925	4	c
4	SBA10	2.86325	4	c
5	SOIL10	1.797	4	d

Analysis of Variance Table for V – Day Twenty

Test: Tukey's HSD
Significance Level: 0.05
Variance: 0.0318911545
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.26915049302
MSD 0.05 = 0.38993149697

Rank	Mean Name	Mean	n	Non-significant ranges
1	BA20	6.82	4	a
2	HBA20	4.36225	4	b
3	SHBA20	2.14125	4	c
4	SBA20	2.06925	4	c
5	SOIL20	1.069925	4	d

Analysis of Variance Table for W – Day One

Test: Tukey's HSD
Significance Level: 0.05
Variance: 13.9044952248
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 5.62001756004
MSD 0.05 = 8.14199459798

Rank	Mean Name	Mean	n	Non-significant ranges
1	BA1	99.4875	4	a
2	HBA1	76.1525	4	b
3	SBA1	20.7575	4	c
4	SHBA1	9.44425	4	d
5	SOIL1	0.08681	4	e

Analysis of Variance Table for W – Day Ten

Test: Tukey's HSD
Significance Level: 0.05
Variance: 2.61047817733
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 2.43511845686
MSD 0.05 = 3.52787533302

Rank	Mean Name	Mean	n	Non-significant ranges
1	HBA10	16.3375	4	a
2	BA10	9.76625	4	b
3	SHBA10	1.1336	4	c
4	SBA10	1.06975	4	c
5	SOIL10	0.1	4	c

Analysis of Variance Table for W – Day Twenty

Test: Tukey's HSD
Significance Level: 0.05
Variance: 1.45763403184
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 1.81963511251

MSD 0.05 = 2.6361944777

Rank	Mean Name	Mean	n	Non-significant ranges
1	BA20	26.525	4	a
2	HBA20	22.6325	4	b
3	SHBA20	0.392525	4	c
4	SBA20	0.3877	4	c
5	SOIL20	0.0923775	4	c

Analysis of Variance Table for Y – Day One

Test: Tukey's HSD
Significance Level: 0.05
Variance: 1.65936185e-4
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.01941469666
MSD 0.05 = 0.02812702161

Rank	Mean Name	Mean	n	Non-significant ranges
1	SOIL1	0.128475	4	a
2	SBA1	0.10171	4	ab
3	BA1	0.1	4	b
4	HBA1	0.1	4	b
5	SHBA1	0.0766225	4	b

Analysis of Variance Table for Y – Day Ten

Test: Tukey's HSD
Significance Level: 0.05
Variance: 1.12180465e-4
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.01596315302
MSD 0.05 = 0.02312660135

Rank	Mean Name	Mean	n	Non-significant ranges
1	BA10	0.1	4	a
2	HBA10	0.1	4	a
3	SHBA10	0.070535	4	b
4	SOIL10	0.06253	4	b
5	SBA10	0.0547025	4	b

Analysis of Variance Table for Y – Day Twenty

Test: Tukey's HSD
Significance Level: 0.05
Variance: 1.1887704e-4
Degrees of Freedom: 15
Keep If:

n Means = 5

LSD 0.05 = 0.01643270468
MSD 0.05 = 0.02380686382

Rank	Mean Name	Mean	n	Non-significant ranges
1	BA20	0.1	4	a
2	HBA20	0.1	4	a
3	SOIL20	0.1	4	a
4	SBA20	0.1	4	a
5	SHBA20	0.06347	4	b

Analysis of Variance Table for Zn – Day One

Test: Tukey's HSD
Significance Level: 0.05
Variance: 0.63933985183
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 1.20510793743
MSD 0.05 = 1.74589887161

Rank	Mean Name	Mean	n	Non-significant ranges
1	BA1	6.7665	4	a
2	SOIL1	3.64225	4	b
3	SHBA1	2.88925	4	b
4	SBA1	2.73575	4	b
5	HBA1	0.351425	4	c

Analysis of Variance Table for Zn – Day Ten

Test: Tukey's HSD
Significance Level: 0.05
Variance: 0.10199204333
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.481330304
MSD 0.05 = 0.69732677757

Rank	Mean Name	Mean	n	Non-significant ranges
1	SOIL10	2.19025	4	a
2	SBA10	1.7975	4	a
3	SHBA10	1.61375	4	a
4	BA10	0.6949	4	b
5	HBA10	0.58065	4	b

Analysis of Variance Table for Zn – Day Twenty

Test: Tukey's HSD
Significance Level: 0.05
Variance: 0.04911719633
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.33402336227
MSD 0.05 = 0.48391599886

Rank	Mean Name	Mean	n	Non-significant ranges
1	SOIL20	1.71125	4	a
2	SHBA20	1.67425	4	a
3	SBA20	1.64425	4	a
4	HBA20	0.695025	4	b
5	BA20	0.597875	4	b

Analysis of Variance Table for Zr – Day One
Test: Tukey's HSD
Significance Level: 0.05
Variance: 0.00170163833
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.06217183549
MSD 0.05 = 0.09007138203

Rank	Mean Name	Mean	n	Non-significant ranges
1	SBA1	0.635075	4	a
2	SOIL1	0.352325	4	b
3	SHBA1	0.2916	4	b
4	BA1	0.1	4	c
5	HBA1	0.1	4	c

Analysis of Variance Table for Zr – Day Ten
Test: Tukey's HSD
Significance Level: 0.05
Variance: 0.00146885583
Degrees of Freedom: 15
Keep If:

n Means = 5
LSD 0.05 = 0.05776298726
MSD 0.05 = 0.08368406775

Rank	Mean Name	Mean	n	Non-significant ranges
1	SHBA10	0.179825	4	a
2	SBA10	0.13745	4	a
3	SOIL10	0.1269	4	a
4	BA10	0.1	4	a
5	HBA10	0.1	4	a

Analysis of Variance Table for Zr – Day Twenty
Test: Tukey's HSD
Significance Level: 0.05
Variance: 1.39734032e-4
Degrees of Freedom: 15

Keep If:

n Means = 5
LSD 0.05 = 0.01781603896
MSD 0.05 = 0.02581096792

Rank	Mean Name	Mean	n	Non-significant ranges
1	BA20	0.1	4	a
2	HBA20	0.1	4	a
3	SHBA20	0.084425	4	ab
4	SBA20	0.0768175	4	ab
5	SOIL20	0.071985	4	b

APPENDIX B1
pH Static Leachate Graphs; n=4.

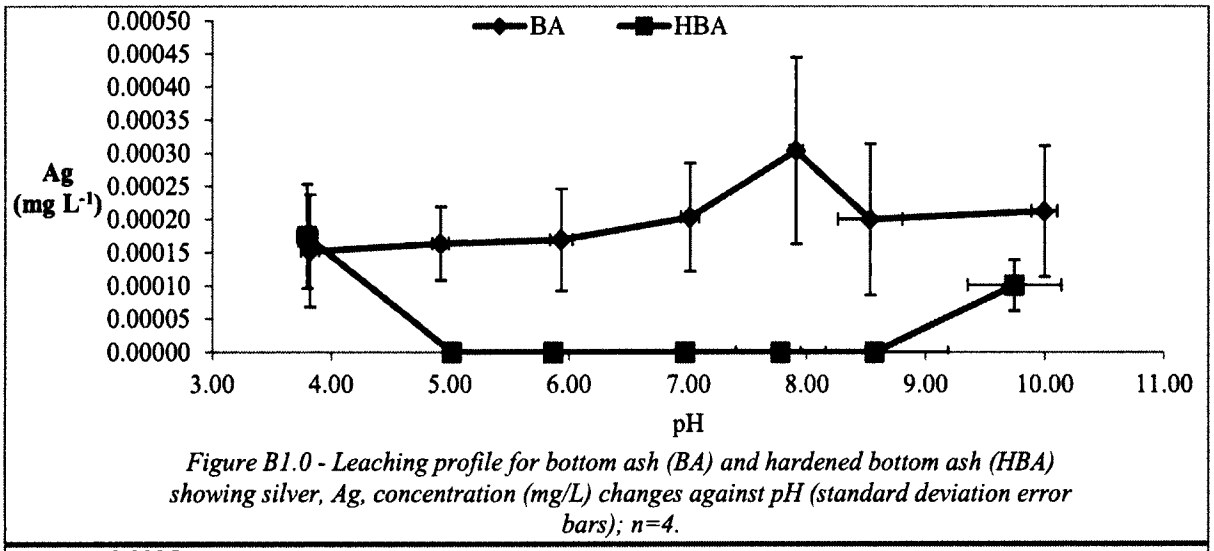

Figure B1.0 - Leaching profile for bottom ash (BA) and hardened bottom ash (HBA) showing silver, Ag, concentration (mg/L) changes against pH (standard deviation error bars); n=4.

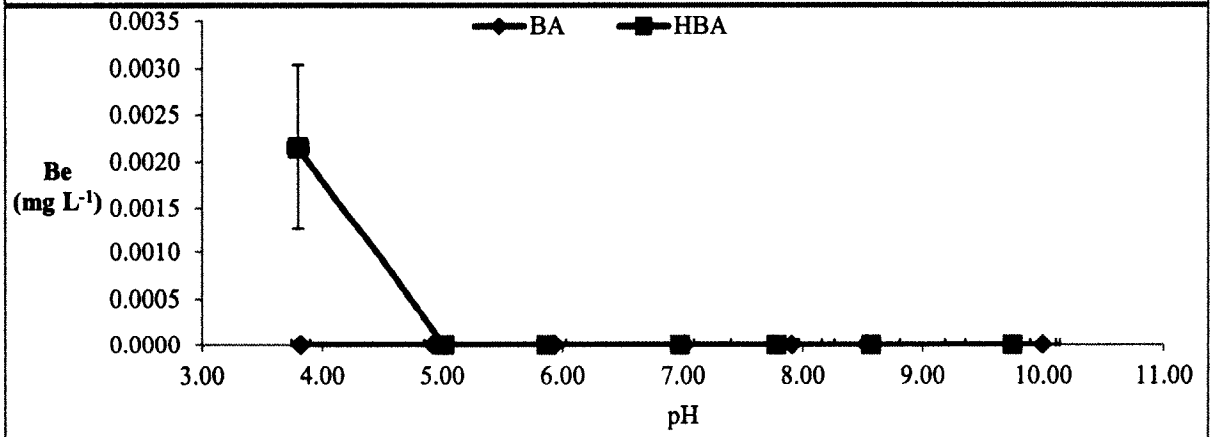

Figure B1.1 - Leaching profile for bottom ash (BA) and hardened bottom ash (HBA) showing beryllium, Be, concentration (mg/L) changes against pH (standard deviation error bars); n=4.

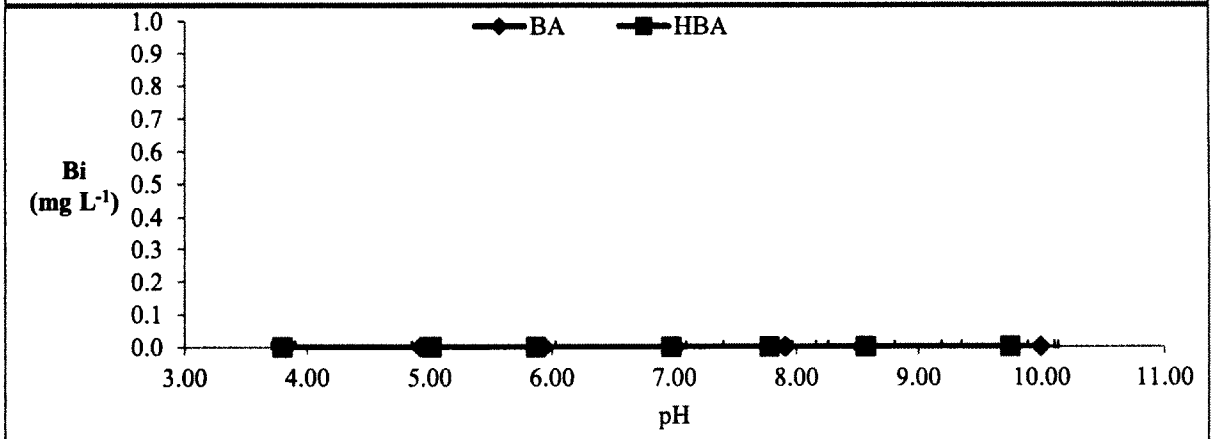

Figure B1.2 - Leaching profile for bottom ash (BA) and hardened bottom ash (HBA) showing bismuth, Bi, concentration (mg/L) changes against pH (standard deviation error bars); n=4.

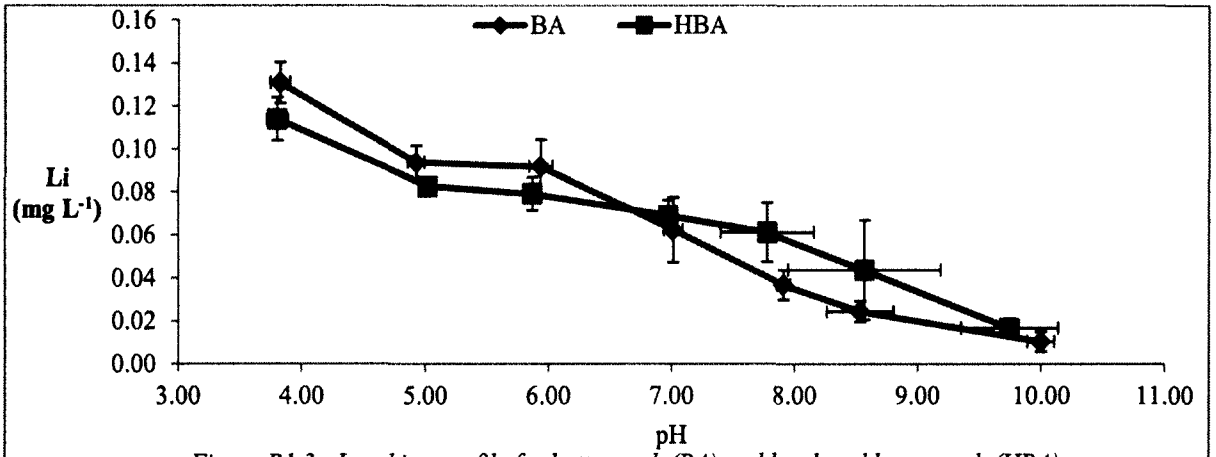

Figure B1.3 - Leaching profile for bottom ash (BA) and hardened bottom ash (HBA) showing lithium, Li, concentration (mg/L) changes against pH (standard deviation error bars); n=4.

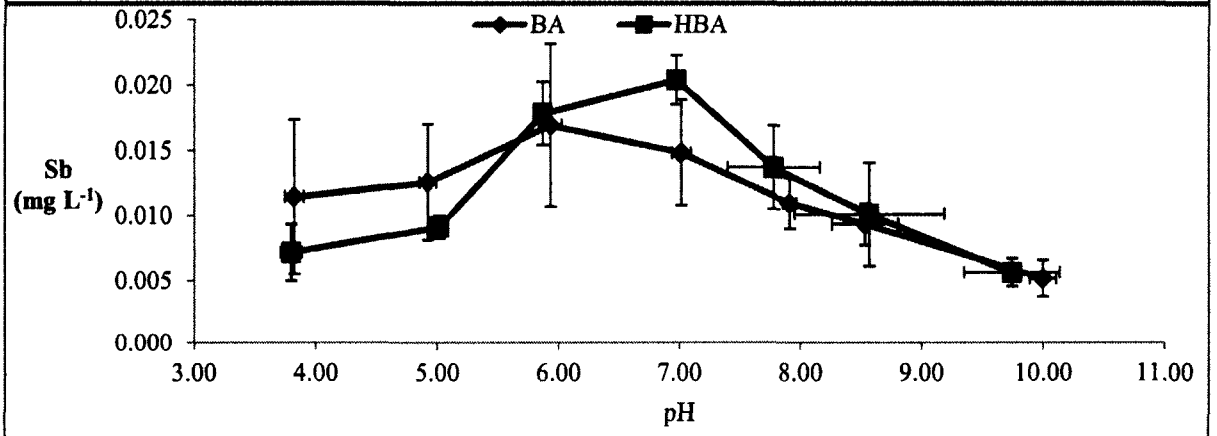

Figure B1.4 - Leaching profile for bottom ash (BA) and hardened bottom ash (HBA) showing antimony, Sb, concentration (mg/L) changes against pH (standard deviation error bars); n=4.

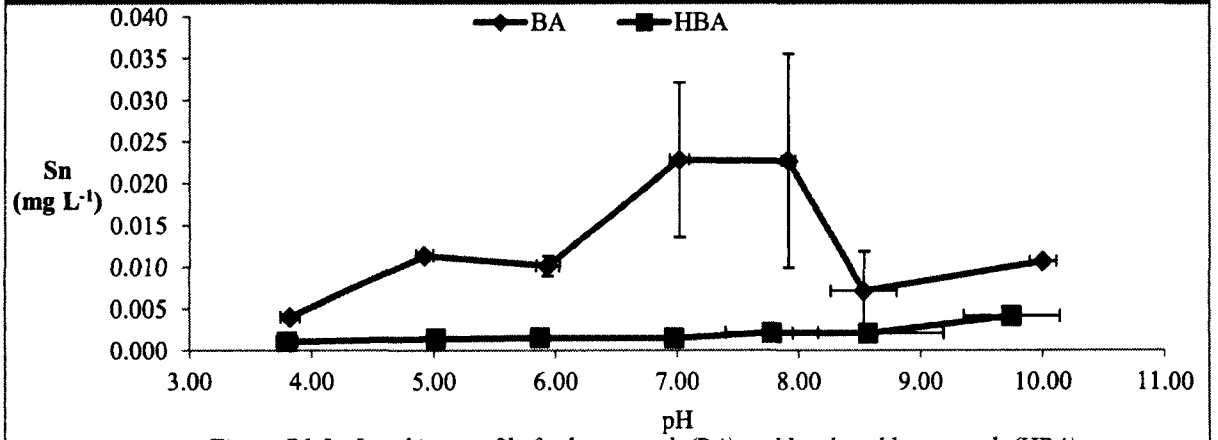

Figure B1.5 - Leaching profile for bottom ash (BA) and hardened bottom ash (HBA) showing tin, Sn, concentration (mg/L) changes against pH (standard deviation error bars); n=4.

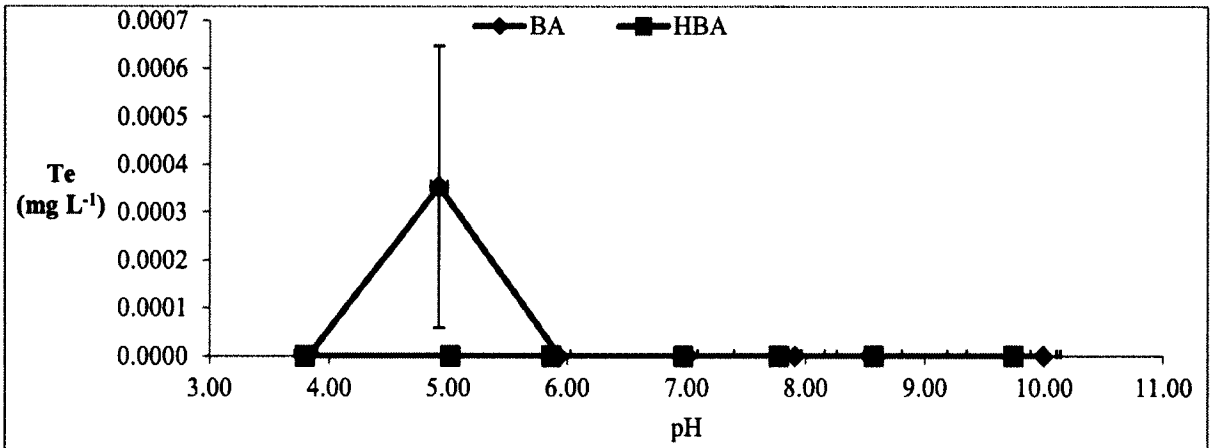

Figure B1.6 - Leaching profile for bottom ash (BA) and hardened bottom ash (HBA) showing tellurium, Te, concentration (mg/L) changes against pH (standard deviation error bars); n=4.

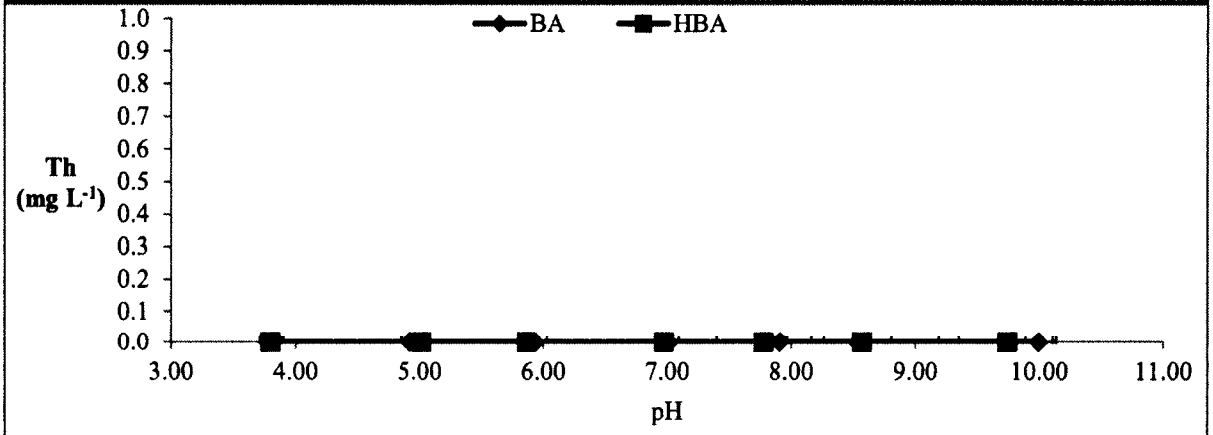

Figure B1.7 - Leaching profile for bottom ash (BA) and hardened bottom ash (HBA) showing thorium, Th, concentration (mg/L) changes against pH (standard deviation error bars); n=4.

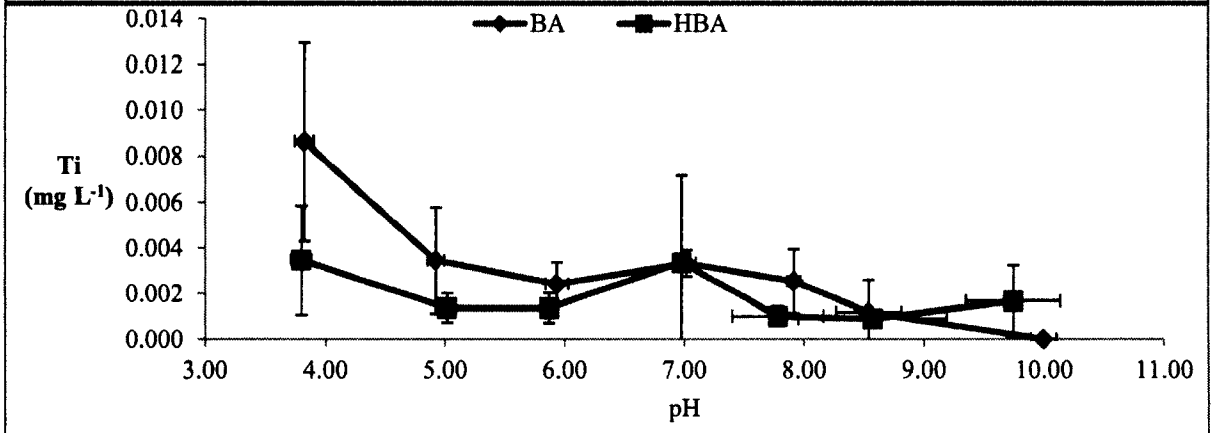

Figure B1.8 - Leaching profile for bottom ash (BA) and hardened bottom ash (HBA) showing titanium, Ti, concentration (mg/L) changes against pH (standard deviation error bars); n=4.

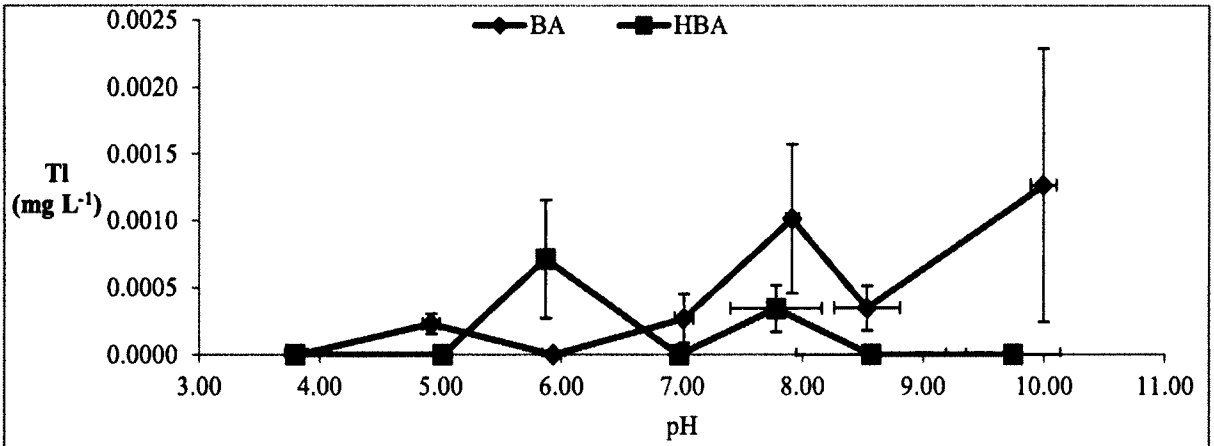

Figure B1.9 - Leaching profile for bottom ash (BA) and hardened bottom ash (HBA) showing tantalum, Tl, concentration (mg/L) changes against pH (standard deviation error bars); n=4.

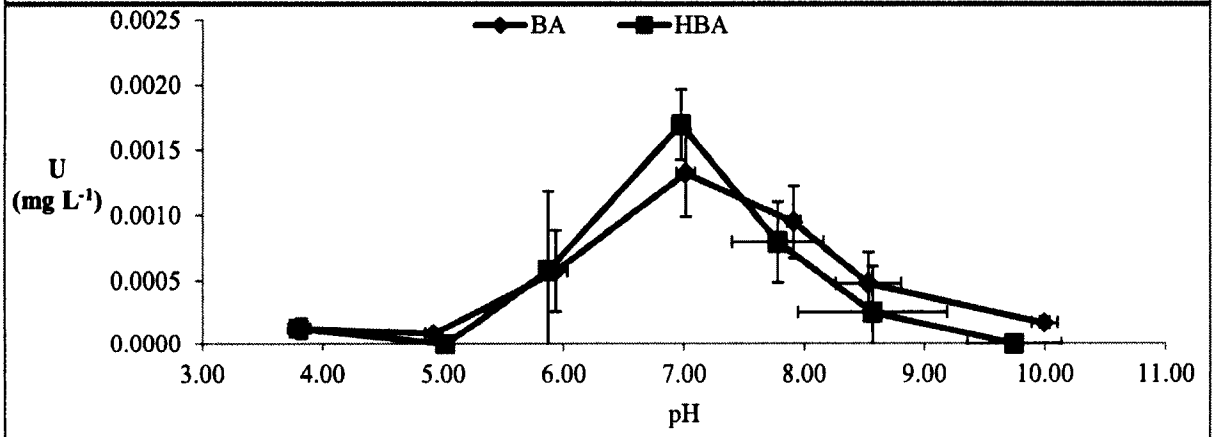

Figure B1.10 - Leaching profile for bottom ash (BA) and hardened bottom ash (HBA) showing uranium, U, concentration (mg/L) changes against pH (standard deviation error bars); n=4.

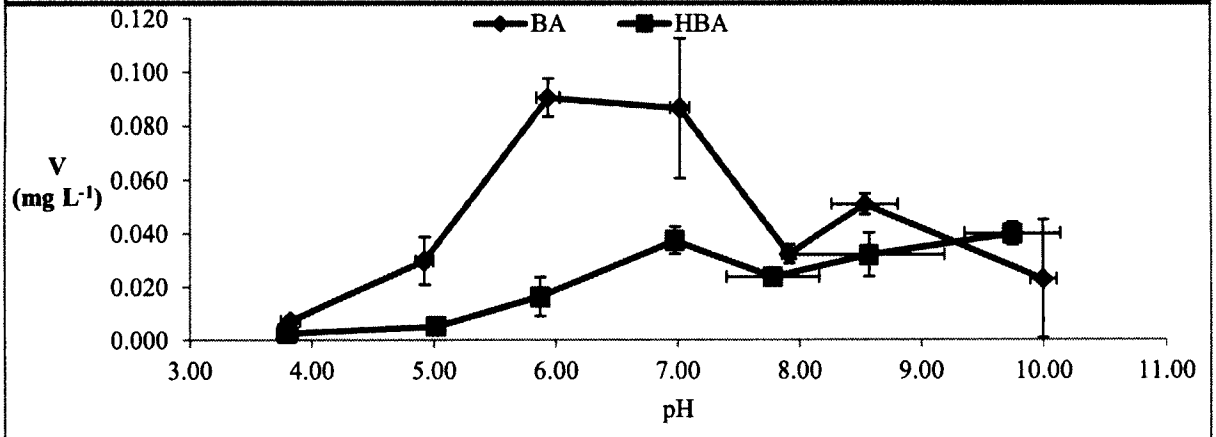

Figure B1.11 - Leaching profile for bottom ash (BA) and hardened bottom ash (HBA) showing vanadium, V, concentration (mg/L) changes against pH (standard deviation error bars); n=4.

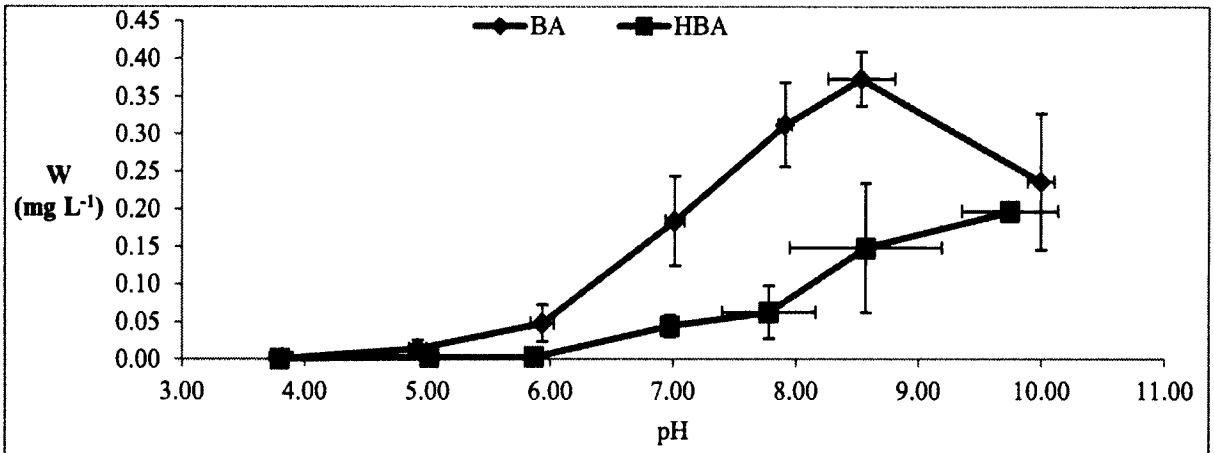

Figure B1.12 - Leaching profile for bottom ash (BA) and hardened bottom ash (HBA) showing tungsten, W, concentration (mg/L) changes against pH (standard deviation error bars); n=4.

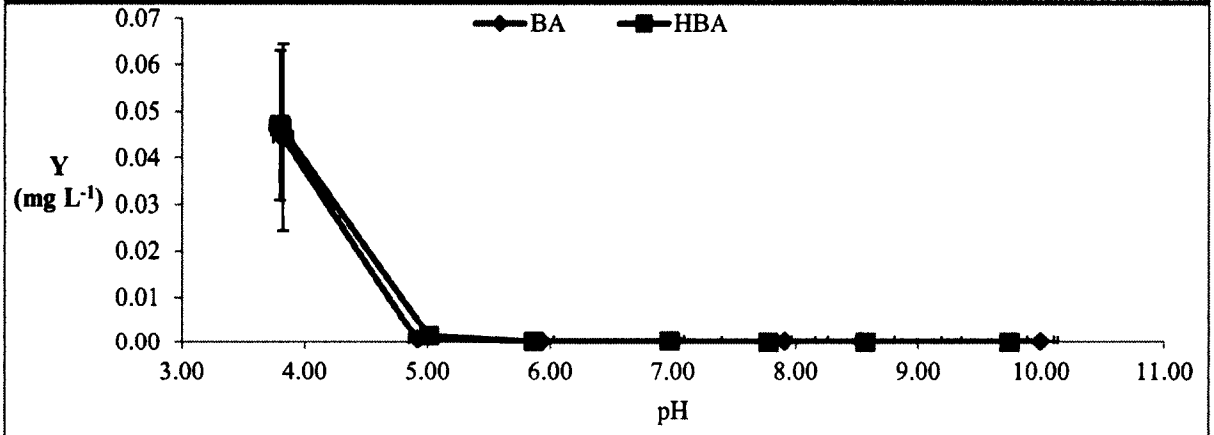

Figure B1.13 - Leaching profile for bottom ash (BA) and hardened bottom ash (HBA) showing yittrium, Y, concentration (mg/L) changes against pH (standard deviation error bars); n=4.

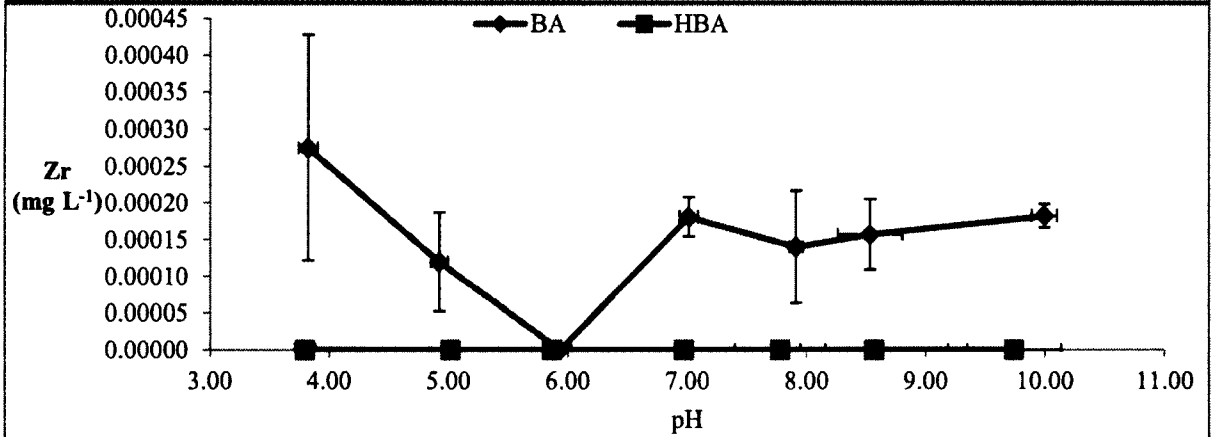

Figure B1.14 - Leaching profile for bottom ash (BA) and hardened bottom ash (HBA) showing zirconium, Zr, concentration (mg/L) changes against pH (standard deviation error bars); n=4.

APPENDIX B2

Mass loss (%) of Indivdiual Elements from Ash During pH Static Experimentation for $HNO_3/HF/H_2BO_3$ Digestion

Table B2.0 – Percentage of elements leached from bottom ash based based on original solid phase concentrations (from $HNO_3/HF/H_2BO_3$ digest) and amount of ash used during pH static experiment for pH 10 to 7.

Parameter (Bottom Ash)	pH 10		pH 9		pH8		pH 7	
	Mean	*SD*	*Mean*	*SD*	*Mean*	*SD*	*Mean*	*SD*
Ag (%)**	0.09	0.05	0.09	0.05	0.14	0.07	0.11	0.05
Al (%)	0.08	0.10	0.0009	0.0005	0.0016	0.0007	0.0018	0.0004
As (%)**	0.19	0.13	1.15	0.50	1.70	0.16	7.78	1.41
Ba (%)	0.47	0.04	0.44	0.01	0.48	0.03	0.49	0.02
Be (%)**	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Bi (%)**	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Ca (%)	19.81	5.34	27.03	0.99	28.71	1.41	38.26	5.79
Cd (%)**	n/a	n/a	n/a	n/a	0.20	0.10	0.25	0.12
Co (%)	n/a	n/a	0.07	0.05	1.67	0.78	1.81	1.13
Cr (%)	1.23	0.50	1.19	0.35	n/a	n/a	0.28	0.34
Cu (%)	0.32	0.03	0.28	0.09	0.45	0.14	0.50	0.17
Fe (%)	0.010	0.000	0.007	0.005	0.02	0.01	0.02	0.01
Hg (%)**	0.09	0.02	0.12	0.01	0.11	0.02	0.08	0.02
K (%)	6.46	0.49	7.57	0.30	7.73	0.39	9.48	0.67
Li (%)	0.51	0.25	1.29	0.27	2.02	0.42	3.85	1.11
Mg (%)	0.46	0.41	6.80	2.37	13.25	5.29	25.78	9.23
Mn (%)	0.001	0.001	0.04	0.03	0.55	0.34	1.29	0.79
Mo (%)	24.59	2.33	31.97	1.21	36.81	2.04	32.13	3.28
Na (%)	2.37	0.56	3.66	0.19	3.92	0.28	6.88	0.95
Ni (%)	0.01	0.01	0.66	0.42	4.93	3.16	9.69	5.97
P (%)	0.02	0.00	0.04	0.02	0.09	0.03	0.68	0.13
Pb (%)**	2.08	0.12	1.62	0.88	2.73	1.23	3.12	1.28
Sb (%)**	0.55	0.16	1.08	0.20	1.31	0.26	1.99	0.64
Sn (%)	0.75	0.05	0.55	0.37	1.81	1.03	2.05	0.89
Sr (%)	12.61	4.72	19.51	0.72	20.04	0.91	26.09	3.49
Ti (%)	n/a	n/a	0.0004	0.0004	0.0008	0.0005	0.0012	0.0003
Tl (%)**	0.26	0.20	0.08	0.04	0.24	0.14	0.07	0.05
U (%)**	0.0036	0.0010	0.01	0.01	0.02	0.01	0.04	0.01
V (%)	0.23	0.23	0.54	0.04	0.36	0.03	1.08	0.38
W (%)	1.07	0.47	1.82	0.17	1.57	0.26	1.02	0.26
Y (%)**	0.02	0.01	0.03	0.01	0.04	0.01	0.06	0.01
Zn (%)	0.08	0.01	0.08	0.01	0.09	0.01	0.18	0.07
Zr (%)	0.0020	0.0002	0.0019	0.0006	0.0018	0.0010	0.0026	0.0005

**n/a designation is given for undetected*

***Estimation based on original detection limit*

Table B2.1 – Percentage of elements leached from bottom ash based based on original solid phase concentrations (from $HNO_3/HF/H_2BO_3$ digest) and amount of ash used during pH static experiment for pH 6 to 4.

Parameter	**pH 6**		**pH 5**		**pH 4**	
(Bottom Ash)	*Mean*	*SD*	*Mean*	*SD*	*Mean*	*SD*
Ag (%)**	0.11	0.05	0.11	0.04	0.11	0.06
Al (%)	0.0021	0.0005	0.02	0.02	1.31	1.27
As (%)**	18.25	2.80	9.82	4.29	0.96	0.49
Ba (%)	0.68	0.10	1.00	0.10	1.39	0.26
Be (%)**	n/a	n/a	n/a	n/a	n/a	n/a
Bi (%)**	n/a	n/a	n/a	n/a	n/a	n/a
Ca (%)	55.39	1.44	65.33	1.98	72.64	2.00
Cd (%)**	0.23	0.06	0.44	0.06	1.20	0.23
Co (%)	5.98	1.00	6.09	1.58	10.84	1.52
Cr (%)	n/a	n/a	0.09	0.06	0.75	0.55
Cu (%)	0.36	0.04	0.49	0.13	6.96	3.07
Fe (%)	0.008	0.001	0.0072	0.0003	0.03	0.02
Hg (%)**	0.05	0.01	0.04	0.01	0.06	0.02
K (%)	11.58	0.83	10.82	0.99	17.15	1.91
Li (%)	6.64	1.01	7.21	0.73	10.87	0.94
Mg (%)	39.73	3.01	44.96	2.44	52.02	1.55
Mn (%)	4.58	0.95	5.50	1.17	14.48	3.06
Mo (%)	21.51	11.93	5.63	4.28	n/a	n/a
Na (%)	9.92	0.74	7.35	0.80	11.42	1.00
Ni (%)	23.33	2.73	33.66	6.45	37.24	1.28
P (%)	3.85	1.00	2.18	0.99	0.29	0.15
Pb (%)**	1.38	0.18	1.55	0.47	0.84	0.04
Sb (%)**	2.64	0.94	2.08	0.69	2.07	1.11
Sn (%)	1.06	0.12	1.26	0.04	0.49	0.07
Sr (%)	38.02	3.33	41.35	1.87	51.15	2.32
Ti (%)	0.0010	0.0004	0.0016	0.0010	0.0042	0.0022
Tl (%)**	n/a	n/a	0.08	0.03	n/a	n/a
U (%)**	0.02	0.01	0.0029	0.0001	0.0046	0.0030
V (%)	1.32	0.10	0.46	0.13	0.12	0.03
W (%)	0.32	0.16	0.10	0.08	0.01	0.00
Y (%)**	0.06	0.02	0.22	0.12	16.09	7.47
Zn (%)	2.05	1.18	12.60	4.83	45.33	4.21
Zr (%)	n/a	n/a	0.0021	0.0012	0.0053	0.0030

**n/a designation is given for undetected*

***Estimation based on original detection limit*

Table B2.2 – Percentage of elements leached from hardened bottom ash based based on original solid phase concentrations (from $HNO_3/HF/H_2BO_3$ digest) and amount of ash used during pH static experiment for pH 10 to 7.

Parameter (Hardened Bottom Ash)	**pH 10**		**pH 9**		**pH8**		**pH 7**	
	Mean	*SD*	*Mean*	*SD*	*Mean*	*SD*	*Mean*	*SD*
Ag (%)**	0.04	0.01	n/a	n/a	n/a	n/a	n/a	n/a
Al (%)	0.0004	0.0002	0.0003	0.0002	0.0002	0.0001	0.0010	0.0011
As (%)**	0.17	0.13	0.55	0.29	1.17	0.17	3.43	0.20
Ba (%)	0.22	0.03	0.41	0.07	0.38	0.05	1.39	1.83
Be (%)**	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Bi (%)**	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Ca (%)	9.50	2.00	15.88	5.10	22.05	4.46	36.60	4.25
Cd (%)**	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Co (%)	n/a	n/a	n/a	n/a	0.15	0.11	0.53	0.33
Cr (%)	1.19	0.37	0.78	0.61	0.62	0.70	0.28	0.12
Cu (%)	0.08	0.00	0.06	0.00	0.06	0.01	0.06	0.02
Fe (%)	0.0017	0.0002	0.0012	0.0001	0.0012	0.0002	0.0019	0.0018
Hg (%)**	0.06	0.01	0.04	0.01	0.03	0.02	0.03	0.01
K (%)	8.84	0.57	10.23	0.78	10.39	0.51	11.19	0.83
Li (%)	0.73	0.22	2.14	1.28	3.17	0.85	4.03	0.53
Mg (%)	1.47	1.76	11.52	7.73	19.95	4.68	26.59	2.26
Mn (%)	0.00	0.00	0.05	0.10	0.15	0.23	0.94	0.56
Mo (%)	18.11	1.12	21.24	1.77	23.50	0.89	23.21	1.61
Na (%)	4.81	0.38	5.98	1.32	7.07	1.34	7.22	1.02
Ni (%)	0.07	0.04	1.24	1.72	2.60	1.72	7.62	1.61
P (%)	0.01	0.01	0.03	0.03	0.08	0.01	0.58	0.09
Pb (%)**	0.31	0.01	0.25	0.06	0.22	0.05	0.19	0.07
Sb (%)**	0.53	0.11	1.07	0.50	1.54	0.43	2.59	0.33
Sn (%)	0.30	0.02	0.17	0.02	0.18	0.01	0.15	0.07
Sr (%)	9.34	1.84	14.23	3.45	18.12	2.90	25.27	2.71
Ti (%)	0.0004	0.0004	0.0002	0.0001	0.0003	0.0001	0.0011	0.0012
Tl (%)**	n/a	n/a	n/a	n/a	0.08	0.03	n/a	n/a
U (%)**	n/a	n/a	0.01	0.01	0.02	0.01	0.04	0.01
V (%)	0.33	0.04	0.29	0.06	0.23	0.04	0.41	0.07
W (%)	1.01	0.06	0.81	0.46	0.37	0.19	0.31	0.10
Y (%)**	n/a	n/a	n/a	n/a	n/a	n/a	0.07	0.05
Zn (%)	0.03	0.002	0.02	0.01	0.02	0.01	0.10	0.03
Zr (%)	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a

**n/a designation is given for undetected*

***Estimation based on original detection limit*

Table B2.3 – Percentage of elements leached from hardened bottom ash based based on original solid phase concentrations (from $HNO_3/HF/H_2BO_3$ digest) and amount of ash used during pH static experiment for pH 6 to 4.

Parameter (Hardened Bottom Ash)	pH 6		pH 5		pH 4	
	Mean	*SD*	*Mean*	*SD*	*Mean*	*SD*
Ag (%)**	n/a	n/a	n/a	n/a	0.12	0.06
Al (%)	0.0007	0.0001	0.0045	0.0040	1.30	0.63
As (%)**	3.53	0.79	1.11	0.39	0.54	0.10
Ba (%)	0.87	0.26	1.73	0.12	1.98	0.23
Be (%)**	n/a	n/a	n/a	n/a	1.50	0.62
Bi (%)**	n/a	n/a	n/a	n/a	n/a	n/a
Ca (%)	58.11	6.74	73.68	3.11	76.62	2.18
Cd (%)**	n/a	n/a	0.28	0.05	0.88	0.13
Co (%)	0.18	0.14	0.83	0.85	4.50	1.06
Cr (%)	0.43	0.12	0.27	0.06	1.05	0.61
Cu (%)	0.08	0.02	0.21	0.07	4.81	1.34
Fe (%)	0.0012	0.0001	0.0016	0.0003	0.0106	0.0039
Hg (%)**	0.05	0.02	0.03	0.01	n/a	n/a
K (%)	11.71	0.91	11.59	0.57	15.19	1.07
Li (%)	5.56	0.75	6.40	0.44	9.18	0.92
Mg (%)	35.77	3.12	44.56	3.42	48.51	0.85
Mn (%)	1.68	0.83	3.59	1.01	10.91	1.66
Mo (%)	5.80	4.19	0.79	0.23	n/a	n/a
Na (%)	8.12	0.96	6.49	0.27	8.68	0.75
Ni (%)	17.13	3.33	25.20	2.50	30.72	1.33
P (%)	1.15	0.24	0.34	0.14	0.29	0.20
Pb (%)**	0.20	0.03	0.17	0.01	0.20	0.05
Sb (%)**	2.70	0.24	1.54	0.13	1.25	0.37
Sn (%)	0.18	0.03	0.19	0.05	0.14	0.03
Sr (%)	36.71	3.93	43.13	2.70	53.74	3.85
Ti (%)	0.0005	0.0002	0.0006	0.0003	0.0016	0.0011
Tl (%)**	0.22	0.13	n/a	n/a	n/a	n/a
U (%)**	0.02	0.02	n/a	n/a	0.00	0.00
V (%)	0.21	0.09	0.08	0.02	0.04	0.01
W (%)	0.03	0.02	0.02	0.00	0.01	0.00
Y (%)**	0.05	0.01	0.51	0.37	16.47	5.74
Zn (%)	1.42	0.82	11.59	5.01	42.11	9.05
Zr (%)	n/a	n/a	n/a	n/a	n/a	n/a

**n/a designation is given for undetected*

***Estimation based on original detection limit*

Table B2.4 - Total elemental content present within the aqueous phase of the blank samples run during pH static experiment.

Parameter	**pH Static Experiment Blanks**	
	Mean	*SD*
Ag (ppb)	<0.1	n/a
Al (ppm)	3.90E-02	3.03E-02
As (ppb)	<0.1	n/a
B (ppm)	8.76E-01	2.51E-01
Ba (ppm)	3.43E-03	1.62E-03
Be (ppb)	<1.0	n/a
Bi (ppb)	<0.1	n/a
Ca (ppm)	1.75E+01	2.83E+00
Cd (ppb)	<0.1	n/a
Co (ppb)	<0.1	n/a
Cr (ppb)	<1.0	n/a
Cu (ppm)	1.63E-02	1.37E-02
Fe (ppm)	1.56E-01	1.90E-01
Hg (ppb)	<0.1	n/a
K (ppm)	1.53E+00	1.57E-01
Li (ppb)	<1.0	n/a
Mg (ppm)	2.95E+00	3.56E-02
Mn (ppb)	<1.0	n/a
Mo (ppm)	3.28E-03	2.22E-03
Na (ppb)	<10.0	n/a
Ni (ppm)	2.12E-03	1.58E-03
P (ppm)	1.85E+00	1.15E-01
Pb (ppm)	3.62E-03	3.82E-03
Sb (ppb)	<0.1	n/a
Se (ppb)	<1.0	n/a
Si (ppb)	<100.	n/a
Sn (ppm)	6.84E-03	7.70E-03
Sr (ppm)	5.51E-02	2.27E-02
Te (ppb)	<0.1	n/a
Th (ppb)	<0.1	n/a
Ti (ppm)	1.36E-03	8.67E-04
Tl (ppb)	<0.1	n/a
U (ppb)	<0.1	n/a
V (ppm)	1.18E-03	3.74E-04
W (ppm)	1.59E-03	1.22E-03
Y (ppb)	<0.1	n/a
Zn (ppm)	4.51E-02	9.72E-03
Zr (ppb)	<0.1	n/a

Sample Percent Loss Calculation for Individual Elements Leached from Ash into the Aqueous Phase (Section 3.3.4); sample calculation for Ca percent loss using one replicate and ICP data following HNO_3/HCl digestion for solid phase.

$Ca\ content\ in\ solid\ phase = 112245mg\ kg^{-1}$
$Amount\ of\ BA\ (OD\ equivalent)\ used\ in\ single\ extraction = 20.0554g = 0.0200554kg$
$Total\ Available\ Ca = 112245mg\ kg^{-1} * 0.0200554kg = 2251mg$

$Aqueous\ Ca\ concentration = 3650mg\ L^{-1}$
$Total\ aqueous\ volume = 0.1213L$
$Total\ Ca\ content\ in\ aqueous\ solution = 3650mg\ L^{-1} * 0.1213L = 443mg$

$$Ca\ Percent\ Loss = \frac{Total\ Ca\ content\ in\ aqueous\ solution}{Total\ Available\ Ca\ content\ in\ solid\ phase} = \frac{443mg}{2251mg} = 19.7\%$$